DIRECTOR OF INDUSTRIES
Bengal.

THE MANUFACTURE OF SULPHURIC ACID AND ALKALI

VOLUME I.—PART II.

THE MANUFACTURE
OF
SULPHURIC ACID AND ALKALI
WITH THE
COLLATERAL BRANCHES

A THEORETICAL AND PRACTICAL TREATISE

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CHAPTER VIII

THE PURIFICATION OF SULPHURIC ACID

COMMERCIAL sulphuric acid, as it is produced in the chambers, always contains a number of impurities, partly owing to the raw material, especially the pyrites, partly to the nitre, the water, the lead of the chambers, etc. Since this acid, if at all, is usually purified at the stage at which we have now arrived, viz., as chamber-acid, before being concentrated, we shall now treat of this subject, although in the great majority of works the chamber-acid is never purified, nor is there any occasion for it. For the sake of completeness, we shall here describe also the manufacture of pure distilled oil of vitriol, although this already presupposes the concentration of acid on a large scale, to be subsequently described.

The impurities of chamber-acid may consist of:—arsenic acid, arsenious acid, antimonic oxide, selenium, thallium, lead, zinc, iron, copper, mercury, calcium, aluminium, alkalies; further, sulphurous acid, nitric acid, nitrous acid, nitric oxide (in the presence of ferrous sulphate), fluorine, organic substances. According to Kuhlemann, for instance (Wagner's *Jahresber.*, 1872, p. 253), the acid of two Harz works contained together with each 100 g. SO_3:—

	a.	*b.*
	g.	g.
Arsenic	0·0088	0·0174
Antimony . . .	0·0394	trace
Copper	0·0013	,,
Iron	0·0081	not estimated
Zinc	0·0087	,,
Lead	trace	0·0231

Most of these substances occur in too small a quantity in the acid to be injurious, and they are also without any influence for most uses of sulphuric acid; the lead, for instance, is almost entirely precipitated on diluting the acid, the iron during its concentration in the platinum still, in the shape of pink crystals of anhydrous ferric sulphate. But there are cases where these impurities may cause trouble. Thus, according to Deutecom (*Chem. Zeit.*, 1892, p. 574), a minute quantity of *mercury* makes sulphuric acid less suitable for pickling brass objects. *Nitric acid* causes wool to be stained yellow in the "carbonising" process. *Platinum* renders the acid unsuitable for electrical storage-batteries. *Iron* sometimes causes a pink colour, which is removed by a little nitric acid, sometimes even by the action of atmospheric air. [This looks as if the pink colour in such cases was not caused by iron, but by selenium.] Sorel (*Fabrication*, p. 414) states that *selenium* is prejudicial to the acid required for parting gold and silver. Drinkwater (*Analyst*, viii. p. 63) holds the same view with respect of the purification of mineral oils. This is confirmed by F. Schultz (*Chem. Zeit.*, 1911, p. 1109). He found that refined, white petroleum when agitated with concentrated sulphuric acid containing SeO_2 turns yellow, all the more so the more acid is employed. In this way as little as 0·005 per cent. SeO_2 can be found in sulphuric acid, by shaking it up with petroleum, which thereby turns black; but nitric or nitrous acid causes this reaction even more intensely. Benzol or benzin (0·730 sp. gr.) do not show it; in the case of petroleum probably an oxidising action takes place.

The only two impurities which cause much trouble for many applications of sulphuric acid are *arsenic* and *nitrogen acids*—the former from a sanitary point of view,[1] the latter owing to the action of the nitrogen acids on the platinum stills; and most methods of purification therefore aim at the removal of these substances. *Selenium* likewise causes trouble in many cases, and we must treat of it as well.

Methods of Purification.

Apart from the cases where impurities are at least partially removed from sulphuric acid in the manufacturing process itself, *e.g.* the constituents of flue-dust by the Glover tower, the iron, the crusts forming in the platinum stills, etc., special purifying processes are sometimes employed either because some impurity (*e.g.* arsenic) occurs in an unusually large quantity, or else because very pure acid is required for special purposes. Different methods must be employed for different cases, but the most important of these refer to the removal of arsenic and to that of the nitrogen compounds. If acid is treated for the removal of arsenic by H_2S, nearly all the other impurities are removed at the same time.

---

[1] We need only point to the "beer-scare" of 1900, consequent upon the mischief done by drinking beer brewed with addition of glucose which had been prepared by means of sulphuric acid with an extraordinarily high percentage of arsenic, some of which remained in the glucose.

Frequently sulphuric acid is *muddy*. A very slight quantity of lead sulphate and especially of selenium may cause this, nor is the muddiness always removed by dust chambers. The removal of the mud is more easily effected, down to a residue of about three milligrams per litre, by making the acid slowly traverse several chambers, if possible in a zigzag direction. At Griesheim the acid is practically clarified by means of a small tower filled with pebbles, but not fed with any liquid, and interposed between the burners and the Glovers; the dirty acid condensing here shows about 85 Tw. Coarser solid matters may be removed by sand-filters, but these frequently do not effect a clarification of sulphuric acid from selenium or other very finely divided substances. This is such a frequent case that many buyers do not object to the turbid appearance of the acid, which in reality does not interfere with its use in the great majority of cases. Good filters for turbid sulphuric acid, capable of making it thoroughly limpid in every case, are not yet known.

The Purification of Sulphuric Acid from Arsenic.

Arsenic is found rarely, and never in more than insignificant traces, in acid which has been made from brimstone: most of the latter material, indeed, is used where acid free from arsenic is wanted. Blende also contains next to no arsenic (*suprà*, p. 110). On the other hand, most descriptions of pyrites contain arsenic, as appears from the analyses quoted in Chapter II., and the acid obtained from pyrites is therefore arsenical, but in very different degrees, according to the percentage of arsenic in the pyrites and to the mode of manufacture.

The percentage of arsenic in pyrites is stated very differently: whilst most analyses of the ordinary ores only show "traces" up to fractions of 1 per cent., H. A. Smith asserts that he has found much larger quantities in the ores most commonly employed, viz., in Westphalian pyrites 1·878, in Belgian pyrites 0·943, in Spanish 1·651, in Portuguese 1·745, in Norwegian 1·649 to 1·708 per cent. of arsenious acid. These analyses are decidedly suspicious since their results differ so much from all others. Nor can we accept his estimations of arsenic in the various products of the alkali manufacture, derived from the original arsenic in the pyrites, his results being extraordinarily high (details in our first edition, p. 462).

Stahl (*Z. angew. Chem.*, 1893, p. 54), in working Spanish pyrites, found in the acid of the first chamber 0·16 per cent. As_2O_3, in the second 0·01 per cent., in the third 0·007 per cent., and in the last chamber only a trace. When working purer pyrites from Virginia or New England, the acid of the first chamber contained 0·005 per cent. As_2O_3, the second nothing, the average 0·002 per cent., all calculated on acid of 66° Bé.

Bräuning (*Preuss. Z. Berg-, etc., Wesen*, 1877, p. 142) states that the chamber-acid made at Oker contains on an average 0·05 per cent. arsenic (and 0·008 per cent. antimony). At Freiberg, in 1880, according to direct information, the chamber acid contained generally 0·02 per cent., but sometimes up to 0·14 per cent. arsenic. Later on we shall see how it stood there in 1902.

Hjelt (*Dingl. polyt. J.*, ccxxvi. p. 174) found in Westphalian pyrites only 0·30, in Norwegian only traces, in Spanish pyrites on an average 0·91 per cent. of As. Of the latter there remained in the cinders 0·19 per cent., in the saltcake none; in the hydrochloric acid: (*a*) pan acid of 38° Tw., 0·066 per cent.; (*b*) drier acid of 32° Tw., 0·014 per cent. This proves that the $AsCl_3$ mostly volatilises in the pan. So far as the sulphuric acid is concerned, Hjelt found, with the same Spanish pyrites, containing 0·91 per cent. of As, for each 100 parts of H_2SO_4, in the

Chamber-acid . . .	0·202	As, of which	0·040	as As_2O_5.
Glover-tower acid . .	0·331	„	0·041	„
Gay-Lussac-tower acid .	0·341	„	0·132	„
Acid of the last chamber . .	0·019			

The higher proportion of the Glover-tower acid comes from the arsenic contained in the gas; the increase of arsenic acid in the Gay-Lussac tower is, of course, caused by the oxidising action of the nitrous vitriol.

I am informed by Mr G. E. Davis that, in 1902, his acid from Rio Tinto pyrites, as it went to the saltcake department 135° Tw. strong, contained on an average 4·83 g. As per litre.

Hehner (*J. Soc. Chem. Ind.*, 1901, p. 188) states the average of As$_2$O$_3$ in ordinary, unpurified pyrites acid = 0·2 per cent. "Purified" acid ought not to contain more than 1 part As$_2$O$_3$ in 200,000 of acid, according to the same authority.

According to G. E. Davis (*Chem. News*, xxxvii. p. 155), in the Glover tower all arsenic acid is reduced to arsenious acid by the burner-gas, and in the Gay-Lussac tower all is again converted into arsenic acid. This assertion is not in accordance with the analyses of Hjelt just quoted, nor with my own analyses, in which I always found both degrees of oxidation of arsenic at the same time.

Filhol and Lacassin found in three samples of "pure" commercial sulphuric acid, per kilogram:—1·2870 g.; 0·5691 g.; traces of As$_2$O$_3$ (Wagner's *Jahresber.*, 1862, p. 212). Further estimations of arsenic in commercial sulphuric acid according to Schnedermann, Kerl, Filhol, etc., will be mentioned later on; those of Kuhlemann have already been given, p. 1039.

Of course, even with the same raw material, the arsenic in the sulphuric acid will vary, according to whether the gas-pipe leading from the burners to the chambers offers more or less opportunity for depositing arsenical flue-dust. In presence of a Glover tower the chamber-acid contains rather less arsenic because a large portion of it is deposited at the bottom of the tower in the shape of mud, but the acid from the tower itsel may occasionally contain all the more arsenic.

At the Freiberg smelting-works, where mixed ores containing from 2 to 2·5 per cent. of As are employed, about 97 per cent. of the arsenic is condensed in the large and well-coole dust-chambers, described pp. 547 *et seq.*, so that the acid contains mostly only 0·02 per cent. of As, only exceptionally up to 0·14 per cent., whilst formerly it amounted to 0·25 or even 0·5 per cent.

The acid made from the very pure pyrites found in some localities in the United States (pp. 83 *et seq.*) is, of course, free from arsenic.

On the *detection* and *estimation* of arsenic in sulphuric acid, cf. *suprà*, pp. 368 and 377.

Injurious Action of the Arsenic contained in Sulphuric Acid.—In most cases where sulphuric acid is employed a small percentage of arsenic is of no consequence—for instance, in superphosphate, or in sulphate of soda to be used for alkali- or glass-making. Probably sulphuric acid, when employed for these operations, is never subjected to a purifying process. In the latter case certainly most of the arsenic passes over into the hydrochloric acid and can be traced there. When the hydrochloric acid is used for generating chlorine, the arsenic does no harm; for although it probably passes over, at any rate partly, into the chloride of lime, it will only occur in this as the insoluble and innocuous calcium arseniate. Much more harm is caused by arsenic in the sulphuric or hydrochloric acid which is employed in the food-industries, for instance in the manufacture of starch-sugar, of tartaric acid, in the fermentation of molasses, for pressed yeast, for washing the regenerated char of sugar-works, etc. A. W. Hofmann has reported a poisoning-case in which bread was contaminated with arsenic by the use of arsenical hydrochloric acid together with soda to make the dough rise. It is unnecessary to speak of medicinal uses, since for them crude sulphuric or hydrochloric acid is never supposed to be employed.

But even for some purely technical uses arsenic in sulphuric (or hydrochloric) acid is not allowable—on the one hand, for the preparation of certain colours, for tinning iron (sheet-iron cleaned with arsenical sulphuric acid is here and there covered with spots of reduced arsenic, which will not take the tin coating—see Gossage in *Hofmann's Report by the Juries*, 1862, p. 12). According to Falding (*J. Soc. Chem. Ind.*, 1906, p. 403) about 150,000 tons of acid 60° Bé. are used in the United States for the pickling of iron previous to galvanising or tinning, and this acid must contain less than 0·002 per cent. of arsenic. No more is arsenic allowable in acid used for the manufacture of preparations which serve for food or medicine, and into which a portion of the arsenic might pass over. To these belong tartaric, citric, phosphoric acids, glucose, milk of sulphur, sulphide of antimony, etc. Even in Doebereiner's lighting-machines arsenical acid must be avoided, since the arseniuretted hydrogen evolved in them would soon spoil the platinum sponge. It has also been observed that ammonium sulphate made from ammoniacal gas-liquor by means of strongly arsenical sulphuric acid turns yellow, no doubt in consequence of the formation of sulphide of arsenic. It is mentioned in our third volume, in describing Deacon's chlorine process, that arsenical sulphuric acid here seems to do great harm also.

Methods of Purification from Arsenic.—In some cases, therefore, it is of importance for the producers of strongly arsenical acid to make it more saleable; and a number of methods of purification have been proposed with this object. None of them seems to produce an acid absolutely free from arsenic, but they do so sufficiently for all practical purposes. Bloxam (*Pharm. J.* [2], iii. p. 606), by employing his electrolytical method for the discovery of arsenic, found that all samples sold as "chemically pure" contained traces of it, and that acid absolutely free from arsenic cannot be obtained in any other way than from pure sulphur dioxide and nitric oxide in glass apparatus at a low temperature, avoiding all cork or india-rubber; the gases themselves must be evolved cold or at a very moderate heat.

Campbell Brown, as well as Towers (*J. Soc. Chem. Ind.*, 1904, p. 221), reports that sulphuric acid dissolves arsenic even out of the glass bottles in which it is stored.

Partial Deposition of the Arsenic in the Manufacturing-process itself.—Hardwick (*J. Soc. Chem. Ind.*, 1904, p. 218) reports a very curious case of the injury caused by burning pyrites with an unusually high percentage of arsenic (1·7 per cent.). Every part of the plant showed the presence of arsenious oxide or acid. The acid from the Glover tower deposited large quantities of As_2O_3 in the shoots, connecting-pipes, acid-eggs, cisterns, and, worst of all, in the Gay-Lussac tower where the coke was ultimately so much choked up with it that the works had to be stopped. After many fruitless attempts to remedy this nuisance, the most effectual method for loosening the deposits of arsenious oxide was found to be the application of steam. To prevent the renewed formation of such deposits, it is not sufficient to allow the Glover tower acid to cool and clarify by settling out the mud. Better results were obtained by heating the acid with strong nitric acid which oxidises the As_2O_3 to As_2O_5, the latter being soluble in strong sulphuric acid. This treatment was carried out in special tanks, provided with a steam-coil for heating and a water-coil for cooling, where the Glover-tower acid, after previous settling out of all the mud removable in such manner, was heated up to 82° C.; the theoretically necessary quantity of nitric acid for oxidising the As_2O_3 to As_2O_5 (as shown by an estimation of the As_2O_3 by means of iodine solution) was added, with good agitation, and the liquor cooled down with occasional agitation. In that way it became possible to work that highly arsenical ore without any stoppages of the plant, at a cost of about 1d. per ton of acid for steam, apart from that of the nitric acid.

The Gräflich von Landsberg Chemische Fabrik, etc. (Fr. P. 432874), oxidises the As_2O_3 in the gases to the non-volatile As_2O_5, which is removed by washing the gases with acid before they enter the chambers. First the dust is removed by filtration through vertical chambers with sloping bottoms, filled with granular material which can be withdrawn below and replenished from above; the gases then pass through one or more Glover towers and then through washing-towers to the chambers, the acid running from the washing-towers being sent finally to the first Glover tower.

Methods for Removing all or nearly all the Arsenic.

The following methods have been employed for the separation of arsenic from sulphuric acid:—

(1) *Distillation* of the sulphuric acid (Bussy and Buignet, *Dingl. polyt. J.*, clxii. p. 454) is said to effect this purpose, even more completely than precipitation by sulphuretted hydrogen, provided that the arsenic is all present as *arsenic acid*, which remains entirely behind in the residue; if, however, arsenious acid be present, it is carried over with the sulphuric acid. Since the sulphuric acid of commerce mostly contains arsenious acid, it should be treated with nitric acid in order to convert all the arsenic into arsenic acid; then the acid must be mixed with a little ammonium sulphate (in order to destroy the nitrous acid) and distilled. In this case the arsenic is asserted to be removed more completely than by sulphuretted hydrogen or barium sulphide; at the same time the dilution of the acid, necessary in the latter case, is avoided. But the distillation of sulphuric acid is an operation somewhat difficult on the large scale, and is not applicable for the purification of chamber-acid.

According to Blondlot (*Comptes rend.*, lviii. p. 76), the mployment of ammonium sulphate is objectionable, because y an excess of it arsenic acid is again reduced. He therefore ecommends heating the acid with peroxide of manganese or otassium permanganate. Bussy and Buignet deny that an xcess of ammonium sulphate reduces arsenic acid (*Comptes end.*, lviii. p. 981). Maxwell Lyte (*Chem. News*, ix. p. 172) ays the statement of Bussy and Buignet, that arsenic does not istil over unless present as arsenious acid, is correct; but in rder to obtain from the first a product completely free from nitrogen compounds, he destroys the latter by adding to the sulphuric acid ¼ to ½ per cent. of oxalic acid, heating in a porcelain dish to 110° C. with continuous stirring, cooling dow to 100° C., and adding potassium bichromate in the state o powder or as a solution in sulphuric acid, till the green colou has been changed to greenish yellow and the presence of fre chromic acid is thus indicated. All the arsenic is no converted into arsenic acid; and on distillation a perfectl pure acid is at once obtained. Permanganate of potas performs the same service, but is more expensive.

The process of Menzies, which will be described in the nex chapter, is asserted to be at the same time a process fo removing the arsenic in the shape of arseniate of iron, but i does so only very imperfectly, as we shall see.

(2) *Removal of the Arsenic by Crystallisation of the Sulphur Acid.*—Morancé (*Comptes rend.*, cxlviii. p. 842) makes use of th fact, established by Lunge, that sulphuric acid of 65°·5 t 65°·8 Bé. crystallises at −20 in a pure state. He concentrate the acid taken from the Glover tower to about 63° B and allows it to stand at a temperature from −8° to + for twenty-four hours, when about half of the acid will hav crystallised out. The crystals are decanted and centrifuge The following table shows the decrease of the impurities b this process:—

	Crystals.	Mother Liquor.
Ash	0·281	0·829
Iron and aluminium	0·029	0·119
Arsenic	0·033	0·388

This shows that anyhow there is no *complete* removal of arsenic effected by this process.

(3) *Removal of the Arsenic as Trichloride.*—The trichloride boils at 125° C.; it is therefore completely volatilised on heating, long before the sulphuric acid has begun to boil: this process can be used without diluting the latter (which is in some cases a great advantage against the removal of the arsenic as sulphide). With this object Otto and Löwe proposed heating the acid with common salt (*Dingl. polyt. J.*, cxxxii. p. 205); Graeger, heating with barium chloride, because the action in this case is not so rapid (*ibid.*, clv. p. 236); Buchner (in 1845) recommended conducting a current of hydrochloric-acid gas into boiling sulphuric acid, and expelling the hydrochloric acid by heating in the open air. Bussy and Buignet have proved that in this way acid free from arsenic cannot be obtained; but Buchner (*Chem. Centr.*, 1864, p. 600) asserts that this is due to the presence of arsenic acid, and that an acid entirely free from arsenic is obtained by first reducing the arsenic acid contained in the sulphuric acid by heating it with charcoal, when the sulphur dioxide evolved causes the reduction; this can also be done when introducing the current of hydrochloric-acid gas. If Buchner's statement is correct, the troublesome operation of distilling the acid is unnecessary. Schwarz (Wagner's *Jahresber.*, 1865, p. 232) heats the acid for some time with 1 per cent. of common salt and ¼ per cent. of charcoal dust under a chimney with a good draught—which comes to the same thing, and appears to be more convenient; but on carrying it out on a large scale great difficulties arise from the fact that the process does not work with dilute acid, and that after the introduction of common salt into concentrated acid the glass retorts often crack. According to Tod (Liebig's *Jahresber.*, 1856, p. 292) if a current of HCl is introduced, heating to 130° to 140° is sufficient, while if common salt be employed the acid must be heated to 180° to 190° C. in order to expel the arsenic trichloride.

Selmi (*Berl. Ber.*, 1880, p. 206) dilutes the acid with half its volume of water, adds some lead chloride, and distils off the first portion, in which all As is contained as $AsCl_3$. Hager (*Chem. Zeit. Rep.*, 1888, p. 234) repeats the same proposal, adding that the employment of chloroform, proposed as useful in this operation, may lead to dangerous explosions. The acid after being decanted from the lead sulphate, is to be submitted to fractional distillation.

In 1905 quite a number of patents was taken out by the United Alkali Company, together with several of their chemists, for the removal of arsenic from sulphuric acid in the shape of arsenious chloride, and the treatment of the latter substance for commercial use (B. Ps. 2916, 7916, 16929, 16930, 16931, 17787, 17886; Amer. Ps. 846288, 863940). The acid is subjected in a suitably packed tower to the action of dry hydrogen chloride gas, at a temperature of about 100°, preferably as it leaves the Glover tower. Arsenious acid may be obtained from the chloride by alkalies or carbonates of various metals. B. P. 5151 of 1906, of Raschen, Wareing, Shores, and the United Alkali Company prescribes reducing arsenic compounds to the arsenious state by charcoal. Their B. P. 23130 of 1906 states that this is a slow process, and the reaction soon ceases owing to selenium depositing on the charcoal. They now overcome this difficulty by subjecting the sulphuric acid to the combined action of HCl, and either sulphur or charcoal at 100° or below. If there is still some deposition of selenium, this may be removed by washing with hydrochloric acid and an oxidising agent, as a hypochlorite or a chlorate. The use of sulphur in connection with HCl is only possible in the absence of selenium; if such is present, charcoal + HCl must be resorted to.

Their Fr. P. 363947 prescribes mixing the arsenious chloride, obtained in the above described manner, with just sufficient water to precipitate the selenium, which is filtered off; a larger quantity of water is then added to precipitate the arsenious oxide.

Raschen, Imison, and the United Alkali Company (B. P. 30196 of 1909) add to the sulphuric acid hydrochloric acid in sufficient quantity to convert the arsenic into chloride, viz., 3 mols. HCl to each molecule of $AsCl_3$, or 5 mols. HCl to each molecule of $AsCl_5$, plus an excess for working losses, and maintain such conditions that the Cl corresponding to the pentavalent As escapes as gas, whilst the $AsCl_3$ remains in the sulphuric acid and is removed by blowing with air.

Crowther, Leach, and Gidden (B. P. 20509 of 1907) remove arsenic and selenium by mixing cold sulphuric acid of 140° down to 135° Tw., with a little hydrochloric acid (30 to 32 per cent.), and bringing it in contact for about two hours with finely divided sulphur, whereby the $AsCl_5$ is reduced to $AsCl_3$, which is then removed by blowing a current of air through the liquid. The process may be worked continuously by passing the mixture of sulphuric and hydrochloric acid down a tower packed with sulphur, a current of air being blown through, or SO_2 may be employed instead of sulphur, by subjecting the mixture of sulphuric and hydrochloric acid to a stream of air containing a small quantity of SO_2. The air carrying the $AsCl_3$ and HCl is first passed into strong hydrochloric acid in order to deposit sulphur and selenium and then into water, to decompose $AsCl_3$ into strong hydrochloric acid and precipitated As_2O_3.

The Verein Chemischer Fabriken, Mannhein (B. P. 16910 of 1906; Ger. P. 179513), takes out the arsenious chlorides by means of hydrocarbons, glycerides, etc., in which it is soluble; especially mineral oils are suitable for this, but not easily decomposable aliphatic glycerides.

The Chemische Fabrik Griesheim-Elektron (B. P. 973 and 974 of 1907; Ger. Ps. 194864 and 195578; Austr. Ps. 32449 and 34022; Belg. Ps. 197391 and 198423; Fr. P. 376934; Ital. Ps. 245/84 and 246/85) convert the arsenic in sulphuric acid into chloride or fluoride and remove it by treating with benzol or derivatives, of this or of aliphatic hydrocarbons, such as dichlorobenzene, or carbon tetrachloride, or acetylene tetrachloride. From these solvents the arsenic is separated by washing with water. For instance, sulphuric acid of 66° Bé. containing 0·1 per cent. As is mixed with 0·6 per cent. hydrochloric acid of 27° Bé., or a corresponding quantity of fluohydric acid; 10 per cent. carbon tetrachloride is added and stirred up with the acid for a few minutes; it is then removed and carries all the arsenic along. When saturated with arsenic, it is treated with twice its weight of water which takes out the arsenic. This treatment is applied at Griesheim to take out the arsenic from Glover-tower acid, upon which great claims are made with respect of colour or smell. It is only applicable to acids over 58° Bé. but does not remove the arsenic from chamber acid, etc. This is, however, effected according to their B. P. 3435 of 1907, by adding, apart from hydrochloric acid, a little iodine or HJ, and then treating with SO_2, which converts the J into HJ; the latter reduces any As_2O_5 to As_2O_3, and the iodine formed acts as before, so that by means of very little iodine up to 80 per cent. of the arsenic can be removed from chamber-acid.

(4) *Removal of Arsenic as a Soap.*—For electrical storage-batteries, sulphuric acid should be as free from arsenic as possible. Arsonval endeavours to attain this by pouring 4 or 5 c.c. of colza oil on to a litre of sulphuric acid, which is to form glycerine-sulphuric acid, and to precipitate the arsenic, lead, etc., in the form of soaps [?]. Gothard prescribes the same addition; the mixture is to be shaken up, allowed to stand for twelve hours, poured into water, and, after cooling, the sticky mud must be skimmed off the purified acid (*Chem. Zeit.*, 1892, p. 163).

(5) *Precipitation of the Arsenic as Sulphide.*—This method, formerly the only one carried out on a manufacturing scale, possesses the advantage that, apart from the arsenic, several other impurities are precipitated (such as lead, antimony, selenium), and others are destroyed (such as sulphurous, nitrous, and nitric acids). Under all circumstances the precipitation must take place at a moderate concentration of the acid; too highly concentrated sulphuric acid is decomposed by sulphuretted hydrogen with separation of sulphur, according to the equation

$$3H_2S+SO_4H_2=4H_2O+4S;$$

the acid must therefore be in the state of chamber-acid, or, better, not above 106° Tw. When the arsenic is present as arsenic acid, it is much more slowly precipitated than when present as arsenious acid.

The simplest way might be thought to consist in generating the sulphuretted hydrogen within the liquid itself; and we shall first consider the methods and proposals made for this purpose.

(*a*) *Precipitation by Barium Sulphide.* — Proposed by Dupasquier in 1845, this process was carried out practically at Chessy (*Hofmann's Report by the Juries*, 1862, p. 12); and it appears to have been used at most of the French works where the acid is purified at all. In this case barium sulphate and sulphuretted hydrogen are formed, the latter being in the nascent state and therefore acting very energetically; this process, has, moreover, the great advantage of leaving nothing soluble behind in the acid. It has been objected that the barium sulphide must be pure and must contain no thiosulphate, since otherwise the well-known decomposition between H_2S and SO_2 with separation of sulphur takes place; this, however, is unfounded, because the barium thiosulphate likewise precipitates the arsenic in the state of sulphide (see below), and only an excess of it (which ought to be avoided in any case) would occasion the above-mentioned reaction. Barium sulphide, according to H. F. Stahl, is most conveniently applied as follows:—The acid is diluted to 76° or 82° Tw., heated to 80° C., and a solution of barium sulphide of 12° Tw. is run in at the bottom of the vessel in such a manner that no H_2S escapes. The As_2S_3 is filtered off on a sand-bed, placed on a layer of quartz lumps, and thus the arsenic is reduced to 0·01 per cent. As. But as the acid on standing in the filter again takes up a little arsenic, it is treated with gaseous H_2S, and is thus reduced to 0·005 per cent. As, which result cannot be attained either with BaS alone or with H_2S, but only by the successive application of each.

(*b*) *Sulphide of iron* may be employed in cases where the iron does no harm—for instance, for acid required in the tinning and galvanising of iron, etc. Its application, however, is very limited.

(*c*) *Sulphide of sodium* is capable of much wider application, although it, too, introduces a foreign substance (sodium sulphate) into the acid; this, however, is innocuous for most uses of the acid. It can easily be made by reducing sodium sulphate with coal; and it must be added to the acid to be purified until no further precipitation takes place. The filtration of the precipitate will be described later on.

(*d*) *Crude calcium sulphide* (alkali-waste) can be used exactly in the same way as sodium sulphide, and with the same drawback of introducing some fixed impurities, since part of the $CaSO_4$ remains in solution.

(*e*) Thomson (Ger. P. 6215 of 1884) employs *ammonium sulphide* for precipitating arsenic and antimony, and at the same time destroying the nitrous compounds in chamber acid. He then filters over finely divided lead, and concentrates in the usual manner.

(*f*) *Sodium and barium thiosulphates* are very much recommended; the latter is more expensive, but leaves nothing soluble in the acid. The following is the reaction which occurs:—

$$As_2O_3 + 3S_2O_3Na_2 = As_2S_3 + 3SO_4Na_2.$$

According to W. Thorn (*Dingl. polyt. J.*, ccxvii., p. 495), the sodium thiosulphate is actually used in some works. Chamber-acid of 106° Tw. is heated to 70° to 80° C., and the necessary quantity of the reagent, either in solution or as powder, is well stirred up with it. The arsenic sulphide is separated in flakes, which soon gather into lumps and sink down to the bottom of the tank; the clear acid is drawn off; and fresh quantities are purified in the same tank, until at last there is too much precipitate collected at the bottom, when it is removed and washed. The operation is very simple; and if an excess of the reagent is avoided, very little sulphur dioxide is evolved. In a particular instance, the average percentage of arsenic in chamber-acid of 106° Tw., before purification, amounted to 0·098 per cent., after purification to 0·004 per cent. The purified acid contains from 0·03 to 0·04 per cent. sodium sulphate, which is harmless for most purposes.

In some cases the presence of sodium sulphate in the acid is objected to, especially when the strongest acid is to be obtained. It is therefore preferable to employ barium thiosulphate, which is easily obtained by mixing moderately concentrated solutions of sodium thiosulphate and barium chloride; most of the barium thiosulphate is precipitated in a crystalline form and is separated from the worthless mother liquor on a vacuum-filter. The acid to be purified is heated to about 80° C., and is well agitated (which can be most readily done by a stream of air), the requisite quantity of barium thiosulphate is thrown in, and the temperature is kept at 80° to 100° till all the arsenic is precipitated. The reaction is:—

$$As_2O_3 + 3BaS_2O_3 = As_2S_3 + 3BaSO_4,$$

so that nothing soluble is left in the liquid. The mixed mud of arsenious sulphide and barium sulphate settles down very rapidly; it is separated from the acid by decantation or filtration and washed in order to remove most of the acid. Where the barium sulphate is of some value, it is easily recovered by boiling the mud with milk of lime, when the arsenic is dissolved, and can be reprecipitated from the solution for sale as "yellow arsenical glass," whilst the residue of barium sulphate can be submitted to the usual treatment for the manufacture of barium chloride. This process is actually carried out on a considerable scale, but it is not quite so cheap as the treatment with sulphuretted hydrogen, and does not seem adapted to acids containing a large quantity of arsenic.

(*g*) *Precipitation by Gaseous Hydrogen Sulphide.*—This process appears first in a patent by W. Hunt (No. 1919 of 1853) and is that which is most usually employed on a large scale.

The older, now obsolete, processes used at Oker and Freiberg are described and illustrated in our first edition, pp. 469 to 473: *cf.* also Knocke, *Dingl. polyt. J.*, cliv. p. 185; Wagner's *Jahresber.*, 1859, p. 145. We here give only the results of Schnedermann's analyses of the acid before and after purification:—

(*α*) Impure acid contained in 10,000 parts—

Sp. gr.	Arsenious acid.	Lead sulphate.
1·832	11·86	3·74
1·837	13·19	2·85
1·836	14·21	5·21

(*β*) After purification, in 10,000 parts—

SO_3	7749·10
H_2O	2243·54
$PbSO_4$ (with traces of $CuSO_4$)	1·72
Na_2SO_4 and K_2SO_4	1·35
$CaSO_4$	0·58
$FeSO_4$	2·91
As_2O_3	0·31
H_2O_3	0·49

The acid was perfectly free from nitrogen compounds. Subsequently, according to Kerl, acid has been obtained containing no more than 3·15 As_2O_3 and Sb_2O_3 together and 11·28 $PbSO_4$ in 100,000 parts.

According to official information obtained by me from the Freiberg Mining Office, the original percentage of arsenic in the ores burnt there averages 2 to 2·5 per cent. As. Ninety-seven per cent. of this arsenic is condensed as flue-dust, and about 3 per cent. gets into the chamber acid, which before purification usually contains 0·02, exceptionally up to 0·08 per cent. As (1902). It is employed in this state in the Gay-Lussac tower or for the manufacture of superphosphate. All other acid is purified, as described below, and then contains only 0·0002 per cent. As_2O_3.

The precipitating-process used more recently at the Freiberg and many other works is described at great length by Bode (*Dingl. polyt. J.*, ccxiii. p. 25; Wagner's *Jahresber.*, 1874, p. 259); the following is an abstract of this, together with some notes I have obtained from Freiberg and taken from actual practice in other places.[1]

1. *Generation of Sulphuretted Hydrogen.*—For this purpose a matte is smelted, consisting principally of ferrous sulphide, FeS, in which at the same time the silver contained in the crude ore is concentrated to the amount of one-third of the original weight. The work was formerly done in a blast-furnace (*cf.* our second edition, p. 643). Now the ferrous sulphide is made in a reverberatory furnace, where per twenty-four hours three or four batches of the following composition are charged: 28 cwt. pyrites (lumps), 8 cwt. old lead slags containing 30 per cent. silica, and 3 cwt. limestone. The consumption of coal is about 4 tons (of good quality), the yield of matte (essentially FeS) is on an average 2½ tons per day.

The matte is broken up into pieces about the size of a fist, and put into the sulphuretted-hydrogen generators; these receive 4 to 5 tons at a time, which lasts eight to ten weeks. Then weak sulphuric acid of 55° to 77° Tw. is added, such as is obtained in washing the arsenic sulphide; later on, the acid may go down to 32° Tw. Each apparatus daily receives 5 cwt. acid of 32° Tw. From 5 tons of matte 7¼ tons of crystallised sulphate of iron are obtained, the manufacture of which from the weak lyes takes place in the usual manner. The generators are represented in Figs. 351 to 359 (pp. 1056 and 1057). They are wooden tanks A and B, made of 3½-in. planks lined with lead and connected by a lead tube *a*. The tank A (5 ft. 6¾ in. square and 5 ft. 2 in. deep) is charged with matte after lifting off the cover, or through the manhole *b*; an india-rubber washer is then put in, and the cover is tightened by thirty screw-bolts. The acid is

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[1] According to official information obtained by me the apparatus and processes described in the text were still at work in 1899, and they would appear to have also been in use in 1902; but a different process, hitherto kept secret, is followed at Aussig.

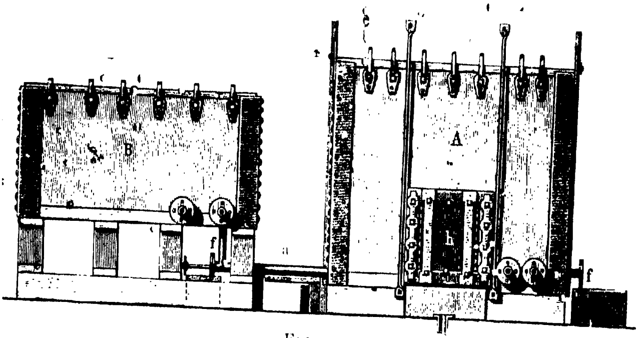

FIG. 351.

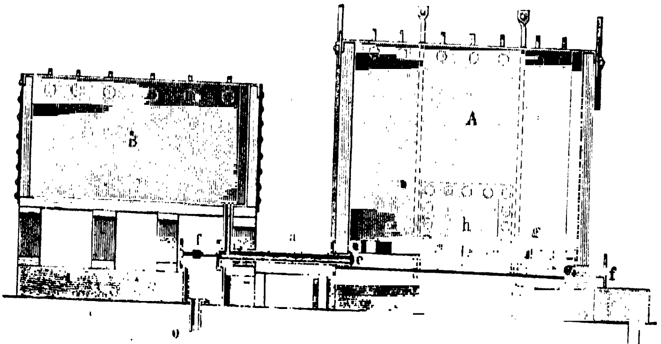

FIG. 352.

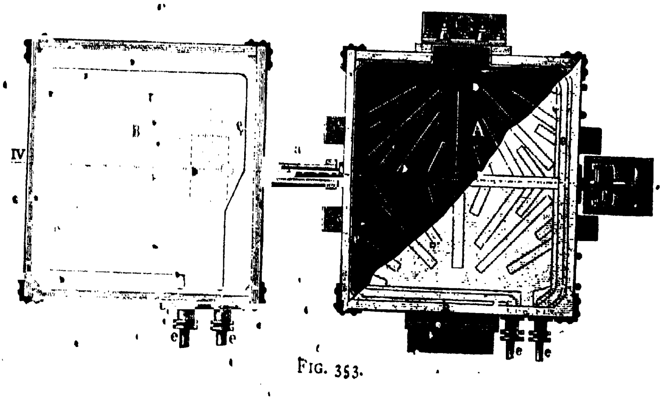

FIG. 353.

un in through a pipe in the cover. B also has a cover, but without an india-rubber joint, as it has only to receive the

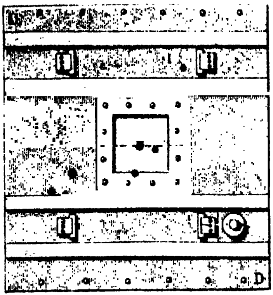

FIG. 354.

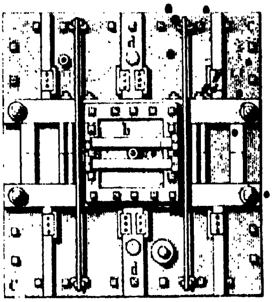

FIG. 355.

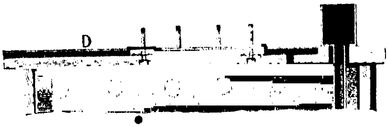

FIG. 356.

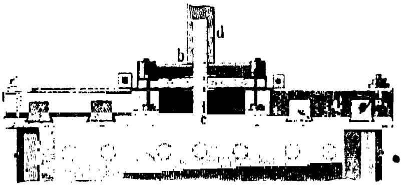

FIG. 357.

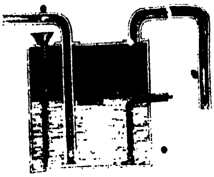

FIG. 358.

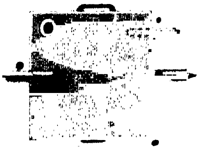

FIG. 359.

solution of ferrous sulphate forced over by the pressure of the gas in the washing-apparatus (Figs. 358 and 359) and the regulating-valves, just as is the case with the ordinary laboratory apparatus. The tank A is very strongly bound with iron, which is coated with lead all over. Steam-pipes, *e*, prevent the ferrous sulphate from crystallising; *f* serves for running the liquor off. On the bottom of A radially placed fire-bricks form a grate (Fig. 353), upon which a lead sieve *g* (Fig. 352) is laid; and the matte lies upon the latter. The lateral manholes *h* permit raking out the residue containing silver. For each 5 tons of chamber-acid on an average 1½ cwt. of matte is consumed.

2. *Precipitation of the Arsenic.*—The chamber-acid of 106° Tw. is treated with H_2S without dilution or heating. The apparatus easily purifies 15 tons of acid daily by a single treatment. It is represented in Figs. 360 to 366 (p. 1059). It consists of a square tower of 5 ft. 4 in. × 5 ft. 6⅝ in. section, and 16 ft. 3 in. available height, which is constructed in the well-known manner with a wooden framework and lead sides of 10 lb. to the square foot. The sulphuretted hydrogen enters at the bottom; the air carried along with it and the steam escape at the top. The tower is filled with 24 tiers of A-shaped inverted lead gutters, 5½ in. high and as wide at the base, made of 10-lb. lead; the lower edges of the gutters have indentations of a tolerably small pattern (Fig. 366). Owing to this, the acid cannot run down in jets, but only in single drops, which, in falling upon the next lower gutter, squirt about and present a large surface to the gas. In each tier there are nine gutters, so arranged that the passage between each two of them corresponds to the upper edge of the gutter in the next lower tier. They are 3 ft. 3 in. long, and laid loosely on leaded ledges on each side, with 1 in. hold on the latter; their vertical distance is 7 in.; the distance between the tiers, therefore, 1½ in. The acid runs in at the cover *l* through nine lead pipes with funnels and regulating-cocks just over each of the lead gutters; there is a hydraulic lute and an oscillating bucket, the details of which are shown in Figs. 365 and 366. The lead gutters should not be burnt fast in the tower, as lumps of arsenic sulphide occasionally get jammed between them. These can sometimes be melted and removed by letting in steam.

The strength of 106° Tw., as indicated by Bode, is rather too high for speedy and complete dearsenication; it is preferable to take the acid only 100° Tw. strong. The process is hastened by employing a slight pressure in the precipitating-tower. This is easily done by not allowing the gas to escape from the top of the tower directly into a chimney, but passing it through a few inches of water, or, preferably, milk of lime, which retains any H_2S not absorbed in the tower.

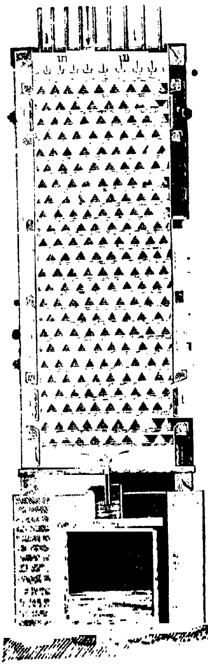
FIG. 360.

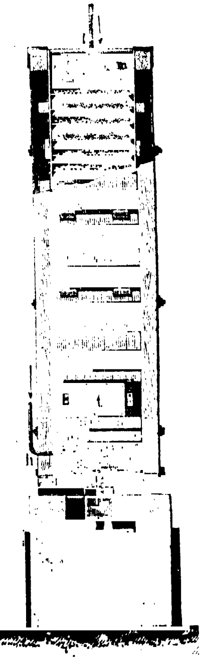
FIG. 361.

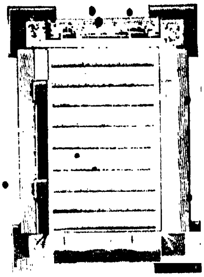
FIG. 362.

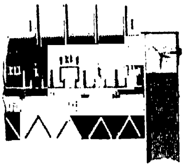
FIG. 363.

FIG. 364.

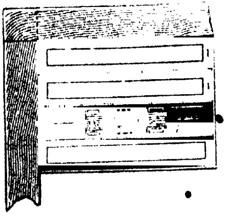
FIG. 365.

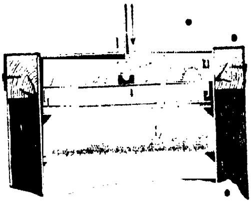
FIG. 366.

Of course constant tests must be made to ensure complete purification in this tower. For ordinary purposes it is sufficient to employ a simplified Marsh test as follows:—Put some of the acid into a 4-oz. bottle, closed with a cork, provided with an outlet-pipe drawn out to a point. A piece of pure zinc is dropped in, the cork is inserted, the gas issuing is lighted (with the ordinary precautions against an explosion by premature lighting if the gas contains air) and the flame is directed on a slab of porcelain, where no spot of As should be produced. For more accurate observations the methods mentioned *supra*, pp. 368 *et seq.*, should be employed. If a batch of acid is not found free from arsenic by the above test, it must be pumped up and treated once more. This test should be repeated by the laboratory chemist before passing a batch as purified, and in cases of any importance the acid should be tested a third time before being sent out. The above simple Marsh test, or the ordinary Marsh-Berzelius test (heating the gas in a tube, where metallic arsenic is deposited), does not detect the minutest traces of arsenic; but it may be taken that any acid in which these tests do not indicate any arsenic is "practically" free from arsenic and can be used for all purposes, like acid made from brimstone.[1]

3. *The filtering and washing of the arsenious sulphide* is a somewhat troublesome operation. At Freiberg, for this purpose a vacuum-filter is used, which is shown in Figs. 367 to 369 (p. 1061). A is the vacuum-retort, B the filtering- and washing-vessel. The former is a small, second-hand steam-boiler of 1 ft. 10 in. diameter and 5 ft. 7 in. length. Steam is conveyed into it through *a* from a boiler; through *b* the air goes away along with the condensed water; and the cock there is only shut when steam has passed through for several minutes. Then *b*, and afterwards *a*, are shut, and the boiler is allowed to cool for some time in order to condense the steam. Then the cock *c* is opened, which connects the vacuum-retort and the space below the filtering-layer in the box B. This box has already been

---

[1] This is universally done, even for the purpose of manufacturing articles of human consumption, in France, Germany, and most other countries, where no brimstone whatever has been used in the manufacture of sulphuric acid for many years past. No inconvenience seems ever to have been caused by this practice in these countries; but since the "beer-scare" of 1900 many people in England demand that no acid should be allowed to be used in the manufacture of articles of food, etc., except that made from brimstone.

filled with the acid to be filtered, whose level is always kept at the same height, lest any cracks be formed in the exposed layer of arsenic sulphide, through which air would enter and destroy the vacuum. By several times shutting & opening *a*

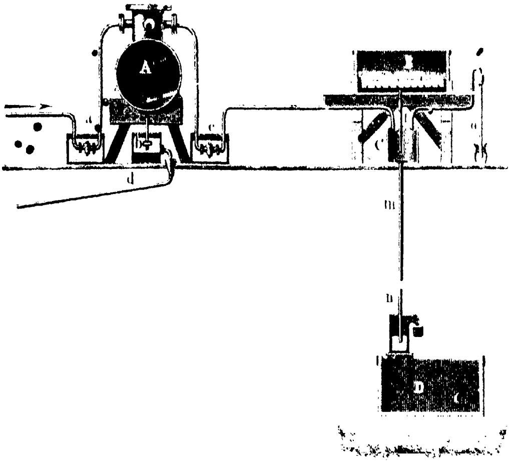

FIG. 367.

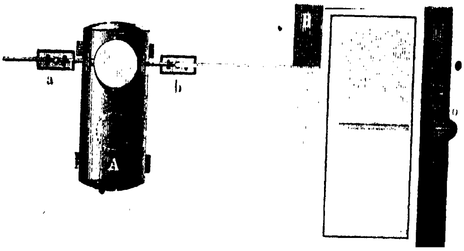

FIG. 368.

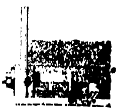

FIG. 369.

and *b*, driving out the air by steam, and cooling down the boiler A, a vacuum of from 10 to 12½ lb. may be obtained. [Probably less steam and labour would be expended if an air-pump were used.] The same vacuum-retort [or air-pump] may work several filters, which can be filled, washed, etc., at will, since the cock *c* permits isolating every one of them.

The filters B are made of 2-in. planks, strengthened at the bottom at *e*, Fig. 369, lined with lead, 4 ft. 4 in. × 5 ft. 7 in. section and 1 ft. 10 in. high. A double pavement of acid-proof fire-bricks leaves a gutter, communicating with the burnt-on pipe *l*. This ends in an intermediate vessel C, whose cover is provided with connecting-tubes for the pressure-gauge *o*, and the vacuum retort A, at *c*; *mn* takes the acid to the receiving-tank D; but the pipe *mn* must be longer than the height of a column of water forced up by the atmospheric pressure, lest the acid should run over into *c*. Over the fire-bricks in B is placed a layer *n* of broken-up quartz (Fig. 369)—pieces the size of a walnut at the bottom, and of finer grain higher up; over this there is a finely perforated sheet of lead, and on the top a layer of powdered arsenic sulphide; the whole filtering-stratum rises 11½ in. above the bottom of the vessel. Where the acid runs in, a piece of lead is placed so as to keep the top layer from being damaged. Every two or three weeks the layers *n* and *m* and the perforated lead plate must be taken out, and the quartz pieces as well as the arsenic sulphide must be rinsed in water. The whole plant requires several pressure-apparatus (acid-eggs) and a good air-pump.

At Oker the work is done very much as at Freiberg (Bräuning, *Preuss. Z.*, *etc.*, 1877, p. 142); but at the former place only that portion of the acid is purified which is not sold to large consumers, especially for superphosphate making. It is there thought best to dilute the acid to 97° to 100° Tw. (*cf.* p. 1058) and to assist the generation of sulphuretted hydrogen by injecting steam at the beginning.

An English patent of M'Kechnie and Gentles (No. 3229 of 25th August 1877) contains essentially the same process as is practised at Freiberg and Oker.

Mr G. E. Davis informed me (1902) that at his works the following process is used for dealing with the arsenious sulphide obtained in purifying O.V. The mud is warmed up to the melting point of naphthalene, paraffin, etc., and a little of these substances is added and the mixture well stirred. Afterwards this naphthalene may be distilled off by steam; if paraffin is used, this may be separated by treatment with ammonium sulphide, or in various other ways.

Riley and Barnes (B. P. 25444 of 1901) recover arsenious acid from the arsenious sulphide by heating it to about 160° C. with nearly its own weight of strong sulphuric acid for some hours. The floating scum of sulphur is removed and washed, and the acid liquor is concentrated to obtain crystallised arsenious acid.

Falding (*Min. Ind.*, viii. p. 583) describes the American practice, where lead-lined boxes are placed in front of a Freiberg tower, as shown in Figs. 360 to 366 (p. 1059). The H_2S gas is forced through the acid in these boxes by means of a perforated pipe on the bottom, and just sufficient acid is run down the tower to prevent the escape of any of the gas. The pipes are connected in such a manner with the boxes that the gas can be made to pass through any one of the boxes first, and that any box can be disconnected from the series. The box so cut out is allowed to rest for a day or two, and the As_2S_3 is settled out so completely that three-quarters or more of the supernatant acid can be decanted without any further treatment. The remaining sludge of As_2S_3 and acid is filtered through broken quartz of graduated sizes in leaden boxes. [This plan requires pumping H_2S against pressure, instead of pumping the acid; the former is probably more expensive than the latter. But the collecting and filtering of the As_2S_3 is undoubtedly less troublesome than in the Freiberg tower.]

Leroy W. M'Cay (*Chem. Ind.*, 1889, p. 371) proposes facilitating the precipitation of arsenic by H_2S by conducting the operation at 100° under pressure and with agitation. The application of pressure for this purpose is also recommended in *Chem. Trade J.*, 1905, xxxvi. p. 135.

Kupfferschläger (*Bull. Soc. Chim.*, xliv. p. 353) dilutes the acid with its own volume of water, treats with SO_2 in order to reduce any arsenic or nitric acid to arsenious or nitrous acid, and then passes H_2S through, which causes all As, Pb, and Se to be precipitated. This proposal he repeats, without any change whatever, in *Monit. Scient.*, 1889, p. 1434.

A special filter for the sulphide of arsenic, as built by Mackenzie and M'Lauchlan, is described in *Chem. Trade J.*, 1908, xlii. p. 67; another, manufactured by S. Bornett & Company, of Cologne, in *Chem. Zeit.*, 1909, p. 119.

Sometimes *explosions* take place during the treatment with hydrogen sulphide. The 41*st Report of the Alkali Inspectors*

(p. 19) says that at certain stages an explosive mixture is formed, and not a few accidents to workmen and to plant have occurred from this cause. This explosive character of the gases is rendered worse by the fact that free hydrogen is given off in the generators from metallic iron contained in the ferrous sulphide employed. Moreover, if either that substance or the sulphuric acid used in the generator contains arsenic, *arseniuretted hydrogen* will be evolved, about the extremely poisonous character of which it is unnecessary to speak.

We will now describe the process of purifying the sulphuric acid from arsenic by means of H_2S, as practised quite recently at one of the very best conducted Continental factories. The chamber acid of 53° Bé. = sp. gr. 1·58 is heated up by steam to 60°, by which process it loses ½° in strength. It is now drawn out of the store-tank by an injector, and in this itself it meets with H_2S, generated as follows: A solution of sodium sulphide on the one side, and sulphuric acid on the other side are aspirated and projected by an injector into a glass flask of merely 5 l. capacity, where, on meeting, they instantly give off H_2S. The evolution of this gas stops at the same moment when the injector is stopped, so that there are never any large quantities of H_2S to deal with. In the injector itself the H_2S acts upon the acid to be purified, and this comes out, with all the arsenic suspended as As_2S_3, up to a mere trace. The purification is purposely not driven beyond 0·005 per cent. arsenic, because sulphuric acid, entirely free from arsenic, acts too strongly on the lead of the concentrating-pans (see p. 1066). The removal of the precipitated As_2S_3 from the clear acid is no easy task. It can be done most efficiently by pouring a little fused paraffin into the muddy acid, stirring up by means of an air-blast. The paraffin forms with the As_2S_3 lumps of the consistency of butter, floating on the surface of the acid and easily ladled off; only an extremely slight trace of paraffin rests behind. The lumps of paraffin + As_2S_3 are treated with a solution of sodium sulphide; the paraffin floats on the top, and can always be used over again. The solution of sodium sulpharsenite is decomposed by sulphuric acid, and the As_2S_3 is now easily filtered off. It is washed, dried, and heated to 150°, which causes it to frit together; in this state it goes out for sale.

In the *Chem. Trade J.*, 1906, xxxviii. pp. 87 to 88, there is a description of the dearsenication of sulphuric acid, with a drawing, which practically agrees with the preceding. We here note merely that the acid is dearsenicated at 110° Tw., and 90 per cent. of it is recovered at 108° Tw., about 10 per cent. at 50° to 60° Tw., by reason of the water used in washing the precipitate. It must not be allowed to get below 100°, or say 105° Tw., as then the iron would be attacked. On the other hand, above 112° Tw. it is difficult to precipitate the whole of the arsenic. The sulphide of arsenic, after washing, in a fairly dry state contains:—

	1.	2.
Arsenious sulphide, As_2S_3	43·02	51·20
Free sulphur	17·03	6·00
Antimonious sulphide	1·11	1·40
Lead sulphide	0·76	0·38
Bismuth sulphide	0·35	0·29
Copper sulphide	0·69	0·22
Ferrous sulphide	1·87	6·02
Calcium sulphate	0·90	0·13
Sulphuric acid	14·20	13·00
Organic substances, insolubles	2·01	6·00
Water, etc.	18·06	15·00
	100·00	99·64

It is very poisonous and should not be put on the waste heap. The small quantity produced at each works sometimes causes a difficulty in utilising it.

According to the same source, p. 90, a sample of ordinary commercial sulphuric acid of 140° Tw. was found to contain:—

	Gram per litre.
Arsenious oxide, As_2O_3	3·18
Arsenic oxide, As_2O_5	2·56
Hydrochloric acid, HCl	0·08
Nitrous compounds, N_2O_3	0·52
Ferrous sulphate	0·56
Aluminium sulphate, $Al_2(SO_4)_3$	0·46
Pb, Zn, Cu, Sb, Bi, Se	traces

In the same journal, 1908, xlii. p. 60, it is stated that the above-described dearsenicating plant is manufactured by Davis Brothers, 66 Deansgate, Manchester, that it has been erected in many works in England, and has been recently further improved.

The evolution of Sulphuretted hydrogen, where no such matte (FeS) as made at Freiberg is obtainable, can be produced cheaply with soda-waste, where an alkali-works is near. Hartmann (Ger. P. 9275) produces this gas by passing pyrites-kiln gas through a cupola furnace filled with red-hot coke. When the temperature has fallen, the current of SO_2 is interrupted and air is blown into the coke till the heat rises again. Or else the impure SO_2 is mixed with the vapours of hydrocarbons and passed through a red-hot retort.

At an American works I found H_2S prepared for the above object from dilute sulphuric acid and sodium sulphide manufactured for this purpose.

Whitehead and Gelstharpe (B. P. 18940 of 1894) obtain H_2S for this purpose by treating liquid from partially oxidised vat-waste with HCl. The mixture thus evolved, containing H_2S, SO_2 [!] and atmospheric air, is said to act better than pure air. [This process is not patentable. The employment of vat-waste for this purpose has been expressly mentioned in this connection in my treatise which appeared in 1891 (*cf.* p. 1066); nor is the partial oxidation patentable, since vat-waste, such as would be available, always has been, and always will be, partially oxidised; nor is it essential whether the waste itself, or the yellow liquor draining from it, is employed. The assertion that SO_2 occurs in these gases at the same time as H_2S is of course wrong, since it is not the question of mere traces. The apparatus described by the inventors presents no specially remarkable features.]

A very curious observation has been communicated to me from a thoroughly trustworthy side, and it is confirmed by the description given, *suprà*, p. 1064. If the treatment with gaseous hydrogen sulphide is continued to the point that the *last trace of arsenic is precipitated* [in which case much free H_2S must be present], *the acid cannot be boiled down in lead pans* without risk of destroying them. Sometimes, not always, this takes place when the concentration reaches sp. gr. 1·63. First a white crust is formed at the line where the acid and the air meet; this eats further down and suddenly the pan falls to powder. If after noticing the first signs the pan is emptied, washed out, and used as a "weak" pan, this will do; but when used as a "strong pan" the destruction goes on even with ordinary acid. [This behaviour reminds one of the sudden conversion of metallic tin into a grey powder which is sometimes observed. Where Kessler ovens are employed for concentrating the dearsenicated acid, *cf.* Chapter IX., the above inconvenience will not be felt.]

The cost of treating a ton of acid for the removal of arsenic may be taken at about 5s. if the ferrous sulphide, etc., has to be bought and the by-products are not utilised. It may be considerably reduced by making ferrous sulphide as above described, or employing some other cheap source of H_2S, and by utilising the ferrous sulphate formed in the process; and if the arsenious sulphide can be sold to advantage, there may be even a slight profit in the purifying operation.

Notoriously much of the acid sold in England as "brimstone acid" is not made from brimstone, but from spent gas-oxide or from pyrites, and is merely dearsenicated in the latter case by sulphuretted hydrogen as described above. Of course this treatment also removes all nitrogen compounds, lead, selenium, copper, etc., so that this acid, if properly purified, is really purer than real brimstone acid, except, of course, as regards iron. The acid coloured brown by the previous processes (especially where the Gay-Lussac tower has been packed with somewhat soft coke) is rendered much lighter in colour by the precipitation of the arsenious sulphide.

Purification of the Sulphuric Acid from Nitrogen Oxides.

Already, when treating of the purification of sulphuric acid from arsenic, it has been stated that mostly by the same operation the nitrogen compounds are removed, and this is always the case when sulphuretted hydrogen is employed for that purpose. In most works, however, no such purification from arsenic takes place; and for most uses of the vitriol the small proportion of nitrogen compounds which it contains is so unimportant that their removal is not called for. In all cases, however, where sulphuric acid has to be concentrated in platinum apparatus, it must be purified as much as possible from nitrogen acids, since otherwise the platinum, as will subsequently be described, would be much more strongly acted upon.

1. *Purification by Sulphur Dioxide.*—Payen has proposed a contrivance for this object. This is a cover over the first boiling-down pan, provided with partitions which force the gas

to travel twice backwards and forwards, and below which the sulphurous kiln-gas circulates. Some manufacturers, instead of this, use pans arched over. This apparatus, however, fulfils its purpose very inefficiently, because the contact between the acid and the sulphur dioxide is very incomplete. The latter object can be attained perfectly in all works where a Glover tower is employed; in this the acid can be fully denitrated and, moreover, a small quantity of sulphur dioxide can be dissolved, in which case, as Scheurer-Kestner has shown (see Chapter IX.), it acts least upon platinum; but, unfortunately, the Glover-tower acid, owing to its large percentage of iron, cannot well be used for concentration in platinum stills.

At some works a small preliminary chamber (tambour) is provided in which there are bottom partitions open at opposite ends, so that the acid entering from the next (large) chamber has to travel a circuitous route long before it arrives at the place where it is drawn off for use. This is done with the object of completely taking the nitre out of the chamber-acid and making it sulphurous, the fresh burner-gas acting upon this acid with full force. Such acid is then employed for concentration in platinum stills. The object of completely removing the nitre (and together with it the selenium) is still better attained by blowing kiln-gases by means of an injector right through the acid in a finely divided stream, and allowing the deposit to settle down by running the acid in circuitous channels.

2. *Treatment with brimstone* has been proposed by Barruel. It is used in the shape of flowers of sulphur, which sometimes, according to Schwarzenberg, is put into boxes of stoneware placed in the first pan, in which the temperature does not rise to the melting-point of sulphur, and in which the acid contains most water. Special care must be taken that no sulphur gets into the following pans, because strong hot sulphuric acid is decomposed by sulphur with the formation of SO_2, and for each part of S $6\frac{1}{8}$ parts of SO_4H_2 are lost. According to Bode (*Gloverthurm*, p. 3) this process is not efficient; while the brimstone is still in the state of powder its action is very slight, although the lead is already being acted upon by the nitrogen acids. Later on, with the rise of temperature, the brimstone melts and rises in small drops to the surface of the hot acid, whence it mostly escapes into the air as SO_2.

3. *Treatment with Organic Substances.*—*Oxalic acid* has been proposed by Löwe. *Sugar* has been suggested by Wackenroder. Skey recommends agitation with *charcoal*, but only for dilute acid (*Chem. News*, xiv. p. 217). Olivier uses a little alcohol in the lead pans (*Rapports du Jury international*, 1867, vii. p. 35).

4. *Ammonium sulphate* has been proposed for this object by Pelouze (*Ann. Chim. Phys.*, lxvii. p. 52), and has been proved to be the best of all reagents. By this reagent the nitrogen acids can be so completely removed that the vitriol is tinted red by the first drop of a solution of potassium permanganate. In this case nitrogen escapes, according to the following equations:—

$$N_2O_3 + 2NH_3 = 3H_2O + 4N,$$
$$2SO_5NH + 2NH_3 = 2SO_4H_2 + 2H_2O + 4N,$$
$$3NO_2 + 4NH_3 = 6H_2O + 7N,$$
$$3NOH_3 + 5NH_3 = 9H_2O + 8N.$$

This substance is now universally employed for acid to be concentrated in platinum stills. Under normal conditions 0·1 to 0·5 lb. of ammonium sulphate suffices for purifying 100 lb. of vitriol.

It appears as if the addition of ammonia was sometimes carried to a ridiculous excess; for Gintl (Wagner's *Jahresber.*, 1880, p. 259) found, in so-called "chemically pure" sulphuric acid, 5 per cent. of NH_3.

Pattinson (*J. Soc. Chem. Ind.*, 1889, p. 706) recommends the treatment with ammonium sulphate for the sulphuric acid employed for generating carbonic acid in the manufacture of aerated beverages, as an extremely small quantity of nitrous acid (0·026 per cent. of N_2O_3) causes the beverage to be turbid, and destroys the pungency of the ginger essence, etc.

Lunge and Abenius (*Z. angew. Chem.*, 1894, p. 609) showed that *nitrous acid* (*i.e.* nitrososulphuric acid) is very quickly destroyed by boiling with a proportion of ammonium sulphate of 1 NH_3 to 1 acid nitrogen; even with sulphuric acid of 140° Tw. this takes place in five minutes. But *nitric acid* is far more stable; it requires half an hour's boiling with its equivalent of ammonium sulphate, in the case of the strongest sulphuric acid, for its destruction, and many hours' boiling with a large excess of ammonium sulphate in the case of acid of 140° Tw. Hence any contamination with nitric acid must be carefully avoided if the sulphuric acid is to be concentrated in platinum vessels, since some HNO_3 will get into the platinum still in spite of all precautions; but nitrous acid is easily removed at every stage by ammonium sulphate.

Selenium.

We have (*suprà*, p. 55) already mentioned selenium as frequently occurring in sulphur and pyrites, and hence getting into the acid-chambers. Its presence in the flue-dust and the chamber-mud are well known; in commercial sulphuric acid it has been found, *e.g.* by Davis (*J. Soc. Chem. Ind.*, 1883, p. 157) and Lunge (*Chem. Ind.*, 1883, p. 128). We shall now go into some detail about it, in which we are greatly aided by a paper of Littmann's in *Z. angew. Chem.*, 1906, pp. 1039 *et seq.* and 1081 *et seq.*

Selenium may cause a temporary or a permanent discoloration of sulphuric acid and may also cause other trouble. As is well known, Se is by nitric acid oxidised only as far as SeO_2, and its solutions are reduced by SO_2 to metallic Se. But in the chambers frequently SeO_2 is found where free Se might be expected, and *vice versâ.* Free selenium exists in several allotropic modifications, of which here the *red* one is of greatest interest, as this is formed in the reduction of SeO_2 by SO_2 at a moderate heat; it then appears as a brick-red powder, or if present in large quantities, as a voluminous jelly. At temperatures above 80° or 90° it passes over into the metal-like *black-grey* modification, apart from a very slight proportion of brown colour, which remains in solution. We also know it in the *colloidal* state, and as a *green* solution in concentrated sulphuric acid.

Selenic acid, $H_2Se_2O_4$, is only formed by the strongest oxidising agents, and is not present in the chambers under normal circumstances; Winteler's assumption to the contrary (*Chem. Zeit.*, 1905, No. 96) is erroneous.

The selenium present in the pyrites at first, of course, burns to SeO_2, but the enormous excess of sulphur dioxide must reduce this to free Se. Yet Littmann always found in the Glover tower, besides free Se, also SeO_2 in varying quantities. The free selenium here appears partly as a dark red sludge, partly dissolved in the Glover acid, to which it imparts a blood-red colour, and from which most of it precipitates with a light red colour on cooling. Most of the selenium, however, according to Littmann, exists in the Glover acid as SeO_2, owing to the presence of small quantities of nitrous compounds which escape the denitrating action of the tower. This SeO_2 is reduced to free Se already by dilution of the acid, and imparts a red colour to it. When employing such red Glover acid on the Gay-Lussac tower, the colour is discharged, all the free Se being converted into SeO_2 by the nitrous compounds. The Glover tower retains at best 20 per cent. of selenium; 80 per cent. or upwards get into the chambers, and is found there first in the red state of free Se, farther on again as SeO_2. The red colour of chamber acid, owing to the presence of free Se, appears in cases where there is too little "nitre" in the chamber, and thus gets into the chamber sludge. The back chambers contain only SeO_2, no free Se, except in cases of extraordinary deficiency of nitre. During the concentration of chamber-acid, which contains both SeO_2 and free Se, the selenium can be partly removed by reducing SeO_2 by an addition of charcoal, but unless it is mechanically removed (which is no easy task), it enters again into solution, and imparts at first a *green* colour to the acid, owing to the formation of the compound $SeSO_3$; when exceeding a concentration of 96·5 per cent. H_2SO_4, the green colour vanishes, SeO_2 being reformed. It is hard to say whether the Se causes more damage in the green acid, or in the more highly concentrated colourless acid, from which it is at once precipitated by dilution. The solution of the Se in form of the green compound begins at 65 and is finished at about 140°; on further heating in the concentrating-apparatus, this compound is again destroyed by oxidation, beginning at 210° and completely at 260 to 280°, and such acid contains only colourless SeO_2. The acid distilling over contains no Se in the first and in the last stage of the concentration, but it does so in the middle stage. Littmann attributes a portion of the damage done to the platinum apparatus in the course of time to the selenium dissolved in the acid. Concentrated sulphuric acid loses its dissolving-power for Se when it is cautiously and with constant cooling diluted to 84·5 per cent. H_2SO_4; hence the hydrate H_2SO_4,H_2O forms the limit.

Littmann draws the following conclusions:—(1) Under the ordinary conditions ruling in the chambers, all modifications o selenium are oxidised to SeO_2, both wherever there is a formation of nitrososulphuric acid, and wherever the latter is principally decomposed by hydrolysis; an excess of SO_2, if present, has no influence. (2) Most of the Se carried on with the chamber gases must be in the state of an intermediary, unstable compound, probably SeO, which is easily reduced to Se or oxidised to SeO_2, according to whether the surrounding gas contains an excess of SO_2, or else of nitrogen oxides. This compound, if combined with SO_2 or SO_3, is more stable and can exist for some time in chamber acid, free from SO_5NH, under certain conditions of concentration and temperature. This SeO has never been prepared in a pure state, but it would explain the presence of selenium in the chamber gases and in many places where neither Se nor SeO_2 can be expected to exist. Selenium exists in the chamber acid also in the shape of sulphonated compounds, which have been studied by a number of chemists, but without leading to quite certain formulæ. Littmann discusses this matter at length, also the conditions for increasing the production of selenium in the chambers, if demand should arise for it, *e.g.* working with as little nitre as possible. The selenium obtained in the Glover or chamber sludge is advantageously prepared in the following way.[1] The sludge is agitated with concentrated sulphuric acid and as much sodium nitrate as corresponds to the selenium it contains; water is gradually added, then steam is injected until the acid goes down to sp. gr. 1·26, and the nitrogen oxides still present are driven out by a current of air. To the filtrate and washings a little HCl or NaCl is added, and the Se is precipitated by a current of SO_2 in the shape of a red jelly, which is washed with water and dried at 105°; it contains about 99 per cent. real Se.

Littmann further discusses at length the *analytical methods* for Se. For proving its presence by qualitative analysis he dilutes the sulphuric acid, adds a grain of KJ, and dissolves the J secreted by $Na_2S_2O_3$; this leaves the Se behind as a red powder, which after a short time passes over into the yellow sulphur compound. Any N_2O_3 or As_2O_3 present do not interfere with this reaction. For quantitative estimations he treats the raw material repeatedly in the water-bath with strong nitric acid, blows a current of air through the hot dilute solution, in order to remove the lower nitrogen oxides, and titrates the solution at a moderate heat with decinormal potassium permanganate, retitrating the excess of this by decinormal oxalic acid. This oxidises the SeO_2 quantitatively to SeO_3. This method is quite correct and very quickly carried out. In the presence of tellurium this is found together with the selenium.

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[1] In *Z. angew. Chem.*, 1906, p. 1329, Deutsch declares that the process described in the text was not worked out by Littmann, but by himself.

As already stated in our former editions, the most usual process for destroying the red colour of sulphuric acid, if due to selenium, is the addition of a little nitric acid, of which, however, any excess is objectionable for many purposes. Therefore Le Roy (*Monit. Scient.*, 1901, p. 406) prefers to add, at a temperature of 50° or 60°, a sulphuric-acid solution of potassium or sodium permanganate, of which at most 10 g. is required for a ton of acid. The pink colour caused by the excess of permanganate is removed by oxalic acid.

F. Schultz (*Chem. Zeit.*, 1911, p. 1129) states that petroleum refined with sulphuric acid containing 0·5 per cent. of selenium has a decided yellow tint in comparison with that purified by pure acid. Selenium dioxide has a greater reaction than the element itself. The coloration is not removed by subsequent treatment of the petroleum with pure acid. Probably the selenium acts as a direct oxidising agent, similar to nitric and nitrous anhydride, which have a similar but decidedly greater action than selenium dioxide.

The recovery of selenium as a commercial product will be described in the chapter treating of the by-products of the sulphuric-acid industry.

Purification of Sulphuric Acid by Special Methods (by Electrolysis, etc.)

According to *J. Franklin Institute*, v. p. 65, lead, iron, and arsenic can be removed by subjecting the sulphuric acid to electrolysis.

Askenasy (Ger. P. 86977) subjects sulphuric acid for some time to electrolysis and allows the products to act upon the acid. Among these is ozone, which destroys organic substances and hydrochloric acid (with formation of chlorine); finely divided sulphur, which reduces the nitrogen compounds; and hydrogen sulphide, which acts in the same manner and also in precipitating any metals present. The latter takes place only with *concentrated* acid. The electrolysis is carried out at ordinary or slightly elevated temperatures, with lead electrodes without diaphragm, and with agitation of the liquid, beginning this after the current has acted quietly for some time. The current-density should be 1 or 2 amps. per square decimetre and the tension 6 volts. After a few hours the acid is colourless; it is then heated up, if necessary, in order to agglomerate the precipitate, or else diluted and afterwards filtered.

Teed (B. P. 17612 of 1887) proposes to remove the *lead* from sulphuric acid by means of hydrochloric acid.

Nicklès removes *hydrofluoric acid* from sulphuric acid by diluting this with twice its volume of water and heating for fifteen hours, replacing the water as it evaporates.

Coloured Acid.

A *brown* colour is so frequently found in sulphuric acid up to about 80 per cent., that the designation "brown oil of vitriol" (B.O.V.) has become universal in England for acid of about 140° Tw. This colour is destroyed during the higher concentration of the acid, and also by the treatment with sulphuretted hydrogen (p. 1067), but not always entirely.

Nörrenberg (*Chem. Ind.*, 1890, p. 363) points out that the *red colour* sometimes found in commercial sulphuric acid of about 140° Tw. may be formed by the contact of that acid, when containing a slight quantity of nitrous acid, with iron tanks. The iron, acting upon the nitrous acid, generates nitric oxide, which is dissolved in the ferrous sulphate formed—thereby producing the red colour. Oxidising agents discharge this colour by converting the ferrous into ferric salt, and the NO into N_2O_3. Completely denitrated acid never assumes the red colour when kept in iron tanks, nor does stronger acid ("rectified oil of vitriol"), which has much less action upon the iron. The same colour may be produced in the small chambers or "tambours" sometimes placed before the first large chamber; here the sulphuric acid is still predominant, and iron is present as flue-dust, so that the conditions are present for the formation of a solution of NO in $FeSO_4$. The main chambers, where nitre predominates, never show that colour, as here all the iron must be present as ferric sulphate.

The red colour, frequently imparted to sulphuric acid by selenium, has been discussed, *suprà*, p. 1071.

A very deeply coloured kind of acid is the *acid-tar* or *sludge-acid*, which will be described more fully in Chapter IX. It is the residue from the acid treatment of mineral oils.

Waring and Breckenridge (Amer. P. 643578) purify this acid-tar by mixing with it, at low temperatures, sodium nitrate in just the quantity required to effect the purification.

The colour of waste acid from *nitrating operations* (nitro-glycerine, gun-cotton, nitro-benzene, etc.) may also be very strong, but this acid is hardly ever sent into trade. It is usually denitrated at the works where it has been obtained, where the colour remaining in the recovered sulphuric acid is of no consequence.

Preparation of Chemically Pure Sulphuric Acid.

Hayes (*Dingl. polyt. J.*, cx. p. 104) proposed to add nitre to sulphuric acid of 152° Tw., coming from the lead pans, sufficient for destroying the largest portion of any hydrochloric acid present, and for oxidising completely the sulphurous and arsenious acids, then to destroy the nitrous acid, etc., again by adding ⅓ per cent. of ammonium sulphate, then to add a little oxide of lead, to allow it to settle in leaden vessels, and to cool the clear acid siphoned off in shallow lead pans down to – 18° C. In this case the hydrate $SO_4H_2+H_2O$ crystallises out; the mother liquor containing all impurities is decanted; the crystals are washed with pure acid, and then form square prisms, sometimes an inch thick and 1¼ in. long. These are fused in clean lead vessels and used as they are, or further concentrated in a platinum still. This process was intended to save the distillation; it has not been successful, however; for it is troublesome and yet does not produce a really pure acid. Exactly the same plan has been proposed by Tjaden-Moddermann (*Z. anal. Chem.*, 1882, p. 218; *Fischer's Jahresber.*, 1882, p. 260).

The only plan for making perfectly pure sulphuric acid for pharmaceutical and analytical purposes is *fractional distillation*, connected with such operations as previously remove the volatile impurities of the vitriol or convert them into fixed compounds. We have seen (pp. 1046 and 1067) how the arsenic and the nitrogen compounds can be removed. We may destroy the latter first by ammonium sulphate, and convert the arsenious acid into non-volatile arsenic acid, or else add a little common salt and reject the first distillate, which contains all the arsenic as $AsCl_3$. It is safer, on account of the danger of spurting, first to remove both nitrogen compounds and arsenic by means of sulphuretted hydrogen; but then the acid must be first much diluted. It never becomes absolutely free from arsenic in this way; it is therefore preferable to employ brimstone acid for rectification.

According to Nicklès, *hydrofluoric acid* can be removed by diluting it with twice its bulk of water and heating it for fifteen hours (*cf.* p. 1074).

The fixed substances, such as iron, lead, copper, etc., remain in the retort on rectifying; and in order to avoid contamination with organic substances, the receiver is changed when about one-twentieth part of the acid has come over; the distillation is interrupted when only one-eighth to one-tenth of the acid is left behind. The portion distilling between these two limits is quite pure.

The distillation of sulphuric acid in glass retorts is a very disagreeable and even dangerous operation, on account of the strong *bumping* caused by the sudden development of large bubbles of vapour; this is especially favoured by the lead sulphate separating. In such cases the retort is sometimes bodily lifted up, and of course smashed when it falls back upon its seat. The bumping must therefore be avoided as much as possible, for which purpose the following plans have been proposed.

Berzelius prescribed heating the retort more from the sides than from below, by placing a sufficiently wide sheet-iron cylinder upon the grate of the furnace, so that the bottom of the retort just fits into it; the coals in the furnace then only heat its sides. In this case, however, the iron cylinder may act as a cracking ring; and A. Müller (*Polyt. Centr.*, 1860, p. 1069) therefore employs an iron pan, in whose bottom a special iron ring protects the retort-bottom from heating, whilst the remaining space of the pan round the retort is filled with fine cast-iron borings. Sometimes the retort is heated in an iron vessel just fitting it, which is generally filled with sand; Reese (*Dingl. polyt. J.*, civ. p. 395) puts ashes on the bottom, as a bad conductor of heat. Frequently, however, the retort is heated by an open fire, and is merely protected by asbestos or by a paste of clay which is continued up to the curve of the neck, so that the vapour is prevented from condensing too soon.

In any case the retorts must be made of very good glass, free from knots, equally thick all over, and not too large; the neck must be protected against draughts, and must not extend to the middle of the receiver, as the latter might be cracked by the hot drops of acid falling into it. It is neither necessary nor advisable to cement the joint between the retort and the receiver, or to cool the latter, considering the high boiling-point of the acid; but it is useful to place a strip of asbestos between the neck of the retort and the receiver, in order to protect the latter against over-heating at the point of contact.

The bumping is very commonly avoided by putting in substances which favour a regular evolution of vapour. For this purpose the following substances may be employed:—platinum scrap or wire, for instance in the shape of spirals; bits of quartz, of porcelain, or of very hard coke. Pelloggio recommended a wide glass tube, drawn out to a fine point at the lower end, and reaching almost down to the bottom of the retort; through this the air can communicate with the interior (*Polyt. Centr.*, 1868, p. 392). Hager has tried this and found it useless. Dittmar conducts a continuous slow current of air through the boiling acid; this expedient has answered very well in my own laboratory.

When distilling about 1 cwt. at a time, it takes from five to six hours of moderately strong heating before the contents of the retort begin to boil; after twelve hours one-twentieth has distilled off. The receiver is now changed; after thirty-six hours (counting from the commencement) the acid is distilled off within one-eighth or one-tenth, and the operation is stopped. According to whether the first change of receiver has been made a little sooner or later, acid more or less concentrated is obtained.

The following method is highly recommended, because the danger of handling such large quantities is thereby avoided. A small tubulated retort holding from a pint to a quart is employed;

above this, a little on one side, a bottle of convenient size is mounted, provided with a glass tap, into which the sulphuric acid to be rectified is put, after it has been freed from all volatile impurities by previous heating. The distillation is now started in the small retort, which is about half filled, and into which a few scraps of platinum are put. Afterwards, by means of the glass tap and of a finely drawn-out glass tube, as much acid is allowed to run continuously from the stock-bottle into the retort as is distilling off. The operation may be continued till too large a quantity of fixed substances is accumulated in the retort. I have seen this plan at work on a small scale in English factories.

Pure sulphuric acid is now attainable in commerce at such a low price that it could not be produced by any of the just described means. It is in reality manufactured from the weak acid distilling over in the production of rectified oil of vitriol (*cf.* next Chapter), which is concentrated by evaporation in glass retorts, or preferably in a small platinum still, to the point required.

Schütz (*Z. angew. Chem.*, 1911, p. 487) again describes this well-known process, without any essential addition of his own.

If acid of 98 per cent. H_2SO_4 is manufactured by concentrating in iron retorts or otherwise, the acid distilling over from the retorts is often of the proper strength of "rectified O.V." (on the Continent and in America = 66° Bé.), viz. 93 to 93·5 per cent. H_2SO_4. If the arsenic has previously been removed, the *distilled* O.V. will be practically pure acid.

In England the designation "rectified oil of vitriol" (R.O.V.) or "distilled oil of vitriol" (D.O.V.) is commonly used, not for distilled sulphuric acid, but for acid concentrated by evaporation to 93 per cent. $H_2SO_4 = 168°$ Tw.

Absolutely pure sulphuric acid is made by Brialle (B. P. 20434 of 1908) by direct oxidation of liquid sulphur dioxide by means of nascent oxygen, obtained by electrolytic decomposition of water. He describes an apparatus adapted to this purpose.

END OF PART II.

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Bengal

CHAPTER VII

THE CHAMBER-PROCESS

Starting the Chambers.

Covering the Chamber-bottom with Acid.—In order to start a set of chambers, first of all the chamber-bottoms must be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into its upstand, as here an hydraulic seal is required to keep the gas within the chamber. Enough liquid for the sides just to dip into it is sufficient; for as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic seal is constantly improving. However, for reasons to be stated hereafter, it is preferable to make the depth of acid as great as possible from the outset. Only in extreme cases *water or very weak acid* should be taken for luting the chamber; acid should rather be bought elsewhere at some expense to avoid this. If it can be done, the proper thing is to bring up the bottom-acid at once to at least about 90° Tw., better 100°. If this cannot be effected, this strength ought at least to be approached as nearly as possible. The reason why starting a chamber with water or very weak acid should be avoided is, that otherwise the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead.

Even if all the nitric acid freshly supplied were decomposed by sulphur dioxide before reaching the bottom, the presence of water or very dilute acid in large quantity would cause the new formation of large quantities of nitric acid from the lower oxides of nitrogen (N_2O_4, N_2O_3, and NO), and, on the other hand, of nitrogen protoxide, N_2O; there would thus be a great loss of nitre in both shapes, apart from the action of the lead, and the reactions within the chamber would be quite irregular.

Altogether the chamber-process only goes on properly when there is an abundant quantity of pretty strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is even preferable to start a chamber dry to starting it with water; but otherwise a layer of about 4 in. of acid on the bottom of such chambers is preferred.

Supposing the chambers to be luted with acid, and the burners to be heated up, so that they can be charged, the connection between them and the chambers is made and the *burner-gas* allowed to enter. Of course sufficient draught is given and nitric acid admitted at once, but at first no steam, in order not to dilute the bottom-acid too much. The *nitric acid* is introduced precisely in the same way as later on, either as vapour or in the liquid form. At first about three or four times as much is put in as is necessary afterwards, because there must be a stock of nitre-gas collected in the chambers, which subsequently needs only to be renewed so far as any loss is suffered. Liquid nitric acid can be introduced much more quickly than gaseous, since the latter depends upon the heat of the burner-gas working the nitre-oven; but running too much nitric acid at once into the chamber must be avoided, since it might not be decomposed entirely before reaching the bottom. This can hardly happen when introducing it through the Glover tower. At the beginning from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, must be employed to 100 parts of sulphur; and this must be continued till the last chamber turns yellow; then the quantity is gradually diminished till the proper point is reached.

MacCulloch (*Chem. News*, xxvii. p. 136) prescribes starting the chambers by admitting steam and nitre-gas from the steam-column (*cf.* p. 849) for five or six hours before the burner-gas is admitted. In that case, he says, the chambers work well from the first, and in one instance showed acid of 1·65 at the drips already in twelve hours. This may be so; but that process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, *steam* is admitted, usually on the second day, but at first with great caution. Then all the factors of acid-making are at work, and the same rules are now valid as for the ordinary process. If everything is in proper order, and if plenty of nitre is used (which is all retained in the Gay-Lussac tower), a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

We must also take into account the opposite case, viz., *when a set of chambers has to be stopped for repairs.* It may be necessary to do so for one or two days, and it is, of course, most important to be able to go on again as quickly as possible, without losing too much nitre. If the proper precautions are neglected, it is possible that so much nitric acid is produced that the chamber-lead is seriously acted upon. To avoid this, we must proceed as follows:—First of all, the pyrites-burners are stopped; no fresh charge is put in, and all openings are closed as tightly as possible. Next to this the supply of nitre is stopped, but that of steam is continued, so long as the gas of the last chamber shows any outward pressure. When this has ceased, and there is, on the contrary, some inward suction, the outlet damper is closed, and air is allowed to enter at some lute, manhole, sight, etc., to avoid forcing-in of the chamber-walls by the atmospheric pressure. Even now a good deal of acid is produced, as proved by the action of the drips; but the steam should be shut off as soon as the drips go down to 100° Tw. When the drips cease to act all openings are shut. If the burners are started again within three days from the stoppage, it is only necessary to put on a good supply of nitre in order to get the chambers to work again; the regulation of the steam must, however, be as carefully attended to as when starting a new set of chambers.

Supply of Air.

The object of a regular chamber-process is of course this:—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. We may add at once, as less decisive, but still of importance, that the chamber-acid should be as strong as is compatible with the two conditions just stated and with preventing damage to the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points, some of which have already been treated of in detail, whilst others will be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brimstone, follows as a matter of course; with pyrites it is much more difficult (*cf.* also pp. 442 *et seq.*).

2nd. *Proper Composition of the Burner-gas.*—This also has been treated of in the 4th Chapter; and we will here merely repeat that the proper composition of the burner-gas almost entirely depends upon the regular supply of air produced by proper *regulation of the draught.* We have already seen (p. 452) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. But at the chambers themselves this must equally be looked to, by means of the man-lids in the top, or the test-plugs (p. 701), or by pressure-gauges or anemometers (pp. 701 and 767). Generally, the following rules may be laid down as a rough guidance:—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue in force whenever a plug is opened. In the middle chamber the gas should be pretty nearly in equilibrium with the outer air; in any case there should be rather a little outward pressure than any inward suction. In the last chamber there may be some, but very little, inward suction; and behind it, but before the damper, the suction should be very perceptible. The Rhenania works (1902) keep some pressure throughout the chambers, diminishing gradually from front to back, the suction beginning only behind the Gay-Lussac, and this is also done at other well-managed works known to the author. Knapp compares the chambers to a lake traversed by a river: the speed of current at its inlet is diminished in the interior of the wide basin so as to be almost imperceptible; but at the outlet in the narrow draught-pipe it again comes out with the same strength as at first. Payen's *Précis* (i. p. 318) states the speed of the gas within the chambers to be 8 to 10 in. per minute. *Cf.* also Niedenführ's measurements of pressures, p. 677.

Generally, it may be said that the draught must be sufficient o cause a proper working of the burners and the proper com-osition of the gas, but *no more than this.* The draught should e observed not merely by practical indications, but by testing he burner-gas for SO_2 and the exit-gas for O. The rule given an here be stated more precisely in this form:—There is so nuch draught given that the burner-gas from brimstone pproaches a percentage of 11 per cent., that from pyrites 8 per ent. SO_2, as far as circumstances permit, and that the gas ssuing at the end still contains 5 or 6 per cent. of oxygen.

A most important control of the working of the chambers, o far as the draught is concerned, is exercised by *testing the xit-gases for oxygen*, as has been described (p. 578), and will be nentioned later on in this Chapter. But there is no agreement n the question as to what is *the proper percentage of oxygen in hamber exit-gases.* Only so far there is general agreement that certain excess of oxygen is required, over and above the heoretical quantity, in order to promote and hasten the egeneration of nitric oxide to nitrous acid, etc. Bode *Beiträge*, p. 15) assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen the yield had been quite as good as, and the consumption of nitre even a shade better than, at 6 per cent. According to Hasenclever (*Hofmann's Report*, i. p. 370), in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from those quoted (*suprà*, pp. 556 and 558) are:—for brimstone,

10·65 per cent. by volume of SO_2,
10·35 " " " O,
79·00 " " " N;

for burning pyrites,

8·80 per cent. by volume of SO_2,
9·60 " " " O,
81·60 " " " N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas = 6 per cent. He has, however, proved that the oxygen in the *burner-gas* is considerably less than according to the above calculation, probably owing to the formation of SO_3 (p. 565).

The above is not universally accepted. Vogt contends (*Dingl. polyt. J.*, ccx. p. 105) that there ought to be only 3 or 4, never above 5 per cent. oxygen in the escaping chamber-gas; oxygen beyond 5 per cent. he calls "very bad work." This opinion is shared by some, but not by many, other practical men. The other extreme is found at a large alkali-works visited by me, where it is believed that the best yield of sulphuric acid is obtained with 10 per cent. of oxygen in the exit-gas, certainly with a somewhat larger consumption of nitre than when 5 or 6 per cent. of oxygen is adhered to (4 per cent. of $NaNO_3$ upon the charge of sulphur, instead of 3 per cent.). The neighbouring works, burning the same pyrites under identical conditions only allow 5 to 6 per cent. oxygen, and I think this decidedly right.

But if it is established that a certain excess of oxygen, although its presence increases the volume of gas, yet also increases the energy of the action in the chambers, it is, on the other hand, at least as well established that too great an excess of air vastly diminishes the yield and seriously increases the consumption of nitre. We here refer to the account of Olivier and Perret's first trials with pyrites (p. 455).

We may assume that in Germany the minimum and maximum of oxygen in the exit-gases is kept between 4 and 8 per cent. In France it is rather lower, say 3 or 4 per cent.; but in England the higher figure 7 or 8 per cent. seems to be preferred in many places. So far as my experience goes, a medium figure, 5 or 6 per cent. oxygen, would in the majority of cases be the proper one to aim at, but, if anything, I would rather allow a margin a little below than above that figure.

Excessive draught acts in a different way, according to whether the admission of air to the burners is regulated in the proper manner or not. If the action of the excess of draught extends to the burners, they will become too hot; sulphur will be sublimed, especially from brimstone-burners, but even from pyrites-burners, and in the latter scars will be formed. If, however, the excess of draught is *very* great, the burners may, on the contrary, become cooled by the excess of air.

If the admission of air below the burner-grates is regulated so that these do not receive too much air, an excessive draught at the end of the system must produce a diminution of pressure in the chambers; air is aspirated through the tiniest chinks and crevices, and in very bad cases the sides of the chamber may be drawn in.

In both cases "false air" gets into the chamber (which means too much oxygen and inert gases), the chamber-space is badly utilised, and the excess of gases carries away both sulphur dioxide and nitrous gases. If the attempt is made to prevent this by employing more nitre, too much work is put upon the Gay-Lussac tower and more nitre will be lost than in a regular way.

In the case of *insufficient draught* at the end of the system there will be too much pressure in the chambers, as the hot gases continue to come over from the burners; after a short time there will be a deficiency of air in these, which is shown by the analysis of the burner-gas and end-gas; the burners first become too hot, as the cooling effect of the air is missing, and scars are formed, whereupon the burners turn cold, the ore burns incompletely, and the gas gets poor. Generally this is accompanied by blowing out of gas from the burners, which might, of course, also be caused by any kind of stoppage in the gas-flue, but cannot be confounded with this contingency, as in this case the pressure in the chambers is not too great, but the reverse. All this again leads to an excessive consumption of nitre, as the lower oxides of nitrogen do not meet with sufficient oxygen, and even NO may go away as such.

Either cause (as a consequence of the above) leads to a bad yield of sulphuric acid, large consumption of nitre, escape of sulphurous acid into the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

In the case of poor ores, and those the sulphur of which is not readily given off, also in the case of burners admitting too much false air, such as the old Belgian burners, too much air gets into the chambers, and the yield is consequently always very bad. At Oker, for instance, in 1859, from a 50-per-cent. pyrites only 100 instead of 300 per cent. of strong acid was obtained, with a consumption of 14·4 parts of nitre to 100 sulphur (Knocke, in *Wagner's Jahresber.*, 1859, p. 148); and the Belgian Commission states, for the four works examined, the yield = 242, 237, 259, and 238 parts, instead of 306 as required by theory. They were able to detect in the escaping gas 0·38 to 1·26 per cent. of sulphur dioxide, and 11·7 to 17·4 per cent. of free oxygen.

The *regulation of the draught* takes place principally or sometimes even exclusively at the exit end by means of the contrivances described (pp. 747 *et seq.*). It is not practicable to depend for this entirely on the ash-pit holes of the pyrites-burners (p. 433), as these must be regulated to suit each individual burner. It is very important not to overlook that the gas-pipe between the burners and the Glover tower and the chamber may be partially stopped up with deposit. In this case the draught at the burner will be bad, but will be little improved by opening the exit-damper ever so wide, and closing the latter will only draw in air at any chance crevice and injure the chamber-process. This cannot be overlooked if the process is properly controlled by regularly testing the burner-gas and exit-gas; if the latter shows enough or more than enough free oxygen while the burner-gas is blowing out, there must be some intermediate stoppage. The lutes or side-plugs, or still better pressure-gauges (p. 777) fixed in various parts of the set will easily allow of localising that stoppage.

On the contrary, some acid makers prefer working in such a way that there is always *ample* draught from the burners into the first chamber, by employing large and very loosely-packed Glover towers; the burners in this case never blow out, and yet the chambers themselves can be worked right to the end with even outward pressure in lieu of inward draught. But there must then be this drawback that, owing to the loose packing, the denitration in the Glover tower will be hardly perfect. This can be obviated by the following plan, which may be usefully adopted in special cases:—The Glover tower is packed as usual, so as to serve as an efficient denitrator and concentrator. From it the gases are still made to ascend a sufficient height, say 6 or 10 ft., in a wide tube, which then turns (avoiding any sharp bends) sideways and dips down into the roof of the first chamber. Thus a siphon is formed, and as the gases in the second descending limb are cooler than in the part rising upwards from the tower (in extreme cases the air-cooling might even be supplemented in summer by water-cooling), this will cause a suction of the gases from the tower, and thus increase the draught from the burners, without drawing the gas away from the chambers too quickly at the other end. Of course this result is much more easily attained by a fan-blast (p. 753).

Exceptionally, air is admitted behind the burners, usually by means of an injector in the first chamber, which is so constructed as to introduce some air together with the steam (p. 743). This must be done where the burner-gases are too rich, and especially where the first supply of air is purposely kept as low as possible, in order to get hotter gas, as, for instance, in H. Glover's brimstone-burner (p. 403), which is intended to concentrate the acid by heat of the gases.

Some chamber-managers contend that no regulation of the draught need take place at the outlet when this has been done once for all, as the outside atmospheric conditions never vary so much as to interfere with the working of the process. But this opinion is decidedly wrong. In most parts of Central Europe the temperature may vary up to 40° C., or even more, between the extreme heat of summer and the extreme cold of winter. But this means that for every 1000 cub. ft. of air required in the coldest season, nearly 1150 cub. ft. must pass through the apparatus in the hottest season, supposing the barometric pressures to be equal. But these latter as well may vary 30 mm., or even more; so that, for instance, 1000 cub. ft. at 760 mm. pressure represent the same weight of air as 1041 cub. ft. at 730 mm. Combining both (and very frequently low temperatures and high barometric pressure go together, as well as high temperatures and a low barometer), 1000 cub. ft. in winter may be equal in weight to 1200 cub. ft. in summer. It is quite evident that such large differences, and even much smaller ones, as they may occur from day to day *must* be compensated by regulating the outlet of the gases accordingly. Nor must it be overlooked that the pressure of wind affects the quantity of gases passing through a given orifice, and this circumstance sometimes during the year has a very serious effect on the draught, even when the burner-house (as it ought to be) is sheltered against the direct action of gusts on the ash-pits.

The great lack of *quantitative* statements as to the draught necessary in various parts of the chamber-system has been partially remedied by an investigation by Nörrenberg (*Chem. Ind.*, 1899, p. 48; *cf.* also the criticism by Eichhorn, *ibid.*, p. 150, and Nörrenberg's answer, p. 237). The required pressure within the chambers can be attained only by a strong up-draught. To produce this, we should make the difference of level between the burners and the Glover tower as great as possible. The gas inlet-pipe from the burners to the Glover tower should rise straight upwards, and should deliver the gases into the tower at the highest practicable temperature. The temperature of the gases leaving the Glover tower should be very little above that of the main-chamber, and any gas to be carried downwards should be cooled as much as possible. The gas leaving the last chamber may descend pretty low towards the Gay-Lussac, which (of course!) produces all the better draught the greater its height and the wider the outlet. The loss of up-draught from the burners should be lessened by giving the connecting-pipes and flues a sufficiently large section for producing the following velocities (having regard to the greatest possible production with normal burner-gases, to the temperature ordinarily attained at the respective places, and the inequalities of work):—

About 0·5 metre per second in the (clean) burner-flues.
„ 1·0 „ „ „ Glover inlet-pipe.
„ 0·8 to 1 „ „ „ Glover grate.
„ 0·25 to 0·5 „ „ „ Glover packing.
(if possible rather less)
„ 1·0 metre per second „ connecting-pipe leading to the last chamber.

The velocity in the pipe leading to the Gay-Lussac and that in the outlet-pipe of the latter should be such that, on deducting all the losses of pressure up to the Gay-Lussac outlet from the effective up-draught, a pressure of 2 mm. water exists at the Gay-Lussac outlet at ordinary temperatures. This is advisable, in order to facilitate the regulation of the final damper. The section of the Gay-Lussac should be equal to that of the Glover tower, or a little less. It should not be made proportional to the quantity of gas at the respective temperatures, on account of the coke-packing. Changes of velocity, curves (especially such with a small radius), and elbows should be avoided as much as possible. By rounding off the edges in the chamber-exits the loss of pressure can be practically avoided.

Hasenclever (*Chem. Ind.*, 1899, p. 27) found in a special case that a Glover tower with good draught showed a pressure of 2 mm. water at bottom and 5 mm. at top; when the pressure was 2 mm. at bottom and 2·5 mm. at top, the tower was found to be obstructed. But he justly points out that no definite figures for the pressure in the various parts of the chamber-apparatus can be stated as a general rule, and that they must be fixed by experience for every special case.

In *horizontal* ducts the loss of pressure can be deduced from the mere observation of the pressure-gauge, but we shall quote a very important remark made to Hasenclever by Dr Drecker, concerning the complication caused by the *difference of level* through the difference of barometric pressure at different heights of the apparatus, neglect of which makes any observations of pressure by a manometer quite unintelligible. Taking the just-quoted example of a Glover tower, showing 2 mm. water-pressure at bottom and 5 mm. at top, but possessing a height of 9·5 m. (about 31 ft.), the difference of atmospheric pressure between the bottom and the top of the tower at 15° C. and 750 mm. mercurial pressure in the barometer is:—

$$\frac{1.294}{1 + \frac{15}{273}} \times \frac{750}{760} \times 9.5 = 11.5 \text{ mm. water.}$$

This we must introduce into our formula, and we thus obtain:

$$11.5 - (5 - 2) = 8.5 \text{ mm.}$$

as the real difference of inward pressure in the tower; that is to say, the pressure within the tower is = 8·5 mm. water higher at the bottom than at the top, and this difference has on the one side to carry the weight of the gaseous column, on the other side to procure the movement of the gases. Taking the specific gravity of the gases = 1·374, and the mean temperature within the tower (350° at bottom, 95° at top) = 222° C., and the outward pressure = 750 mm. mercury, we find:

$$\frac{1.374}{1+\frac{1}{273}\times 222}\times\frac{750}{760}\times 9.5 = 7.10 \text{ mm. water}$$

or a pressure of 7·10 kl. per square metre. The difference 8·5 − 7·10 = 1·40 indicates the pressure, in terms of millimetres of water-pressure, which causes the ascending movement of the gases.

If we call the difference of weight between a gaseous column and a column of air of equal height its *upward stress* or *buoyancy*, in the present case 11·6 − 7·10 = 4·40, we find the *loss of pressure* between two points in the system to be equal to the observed manometric difference of pressure *plus* the buoyancy; in the present case: observed manometric difference (−3) + buoyancy (+4·40) = 1·40 *loss of pressure in that special Glover tower*, caused by frictional resistance between its bottom and top, etc. If the tower were obstructed by deposits, this loss of pressure would become greater, and we can by similar calculations establish for any given apparatus and by special observations the best conditions to be aimed at, but we should commit a great mistake if we attempted to lay down a general rule for all cases from such special observations.

In this case, as well as in well-nigh every other case in chemical manufacturing, it is entirely premature to apply apparently exact mathematical formulæ as a general guide for actual practice, which Sorel has done by applying to vitriol-chambers Clegg's formulæ for the movement of gases in pipes. The extraordinary complication of the case, caused by the sudden expansion of pipes into the enormously larger section of chambers, by the sharp angles through which the gases must sometimes be conducted, by the changes of temperature, and by the chemical reactions which cause alterations in the volume of the gases and vapours, etc., etc., make the application of any simple formula quite illusory. These formulæ may overawe those who are ignorant of mathematics, especially when they contain the (for such people) mystic symbols of higher mathematics, but I know absolutely of no case in the whole range of manufacturing chemistry where the least practical progress has been made by applying complicated mathematical formulæ to chemical operations. The time for this may come in the (probably somewhat distant) future, when the *elements* necessary for such calculations have been thoroughly studied and placed on a secure *experimental* basis.

Supply of Water (Steam).

The regulation of the steam or water-spray is one of the most important parts of chamber-management, and should always be taken in hand by the responsible foreman or superintendent himself. One of the first conditions for enabling him to do so properly is that the tension of the steam should be kept as nearly equal as possible; and it is hardly necessary to point out how much this task is facilitated by a registering steam-gauge or by automatically regulating steam-valves (pp 713, 725). The round of the chambers should be made two or three times a day; at some works it is even made every other hour. It is one of the advantages of the water-spray system (pp. 728 *et seq.*) that there are hardly any variations of the quantity of water supplied, but other difficulties may occur instead (p. 731).

It must be borne in mind that the Glover tower supplies the first or "leading" chamber of a set with a good deal of the steam required. Hence steam or water-spray must be supplied to this chamber in much smaller quantity than when working without a Glover tower, and the position of the jets is also influenced by this (*cf.* p. 725).

A rough indication of the fact, whether too little or too much steam is present, is sometimes sought in the appearance of the glass jars covering the two lutes of the chambers (p. 701). If these show a white crystalline covering of chamber-crystals, which are proved as such by turning green on moistening them, there is evidently a deficiency of steam. If, on the other hand, the glass jars are dripping wet, there is too much steam in the chamber. This is, of course, only to be taken in conjunction with the other observations to be made by the attendant.

The proper indicator for the admission of steam or water is the *strength of acid made in the chamber*, both as observed in the acid-drips (p. 698) and in the bottom-acid. These two are never identical; the drip-acid is always more or less stronger than the bottom-acid. In long chambers there is a considerable difference between the front and the back part, and such chambers should be provided with two or even more different sets of drips.

Considerable difference of opinion exists as to the *strength of acid* most conducive to a proper working of the vitriol-chambers—that is, to the best yield, the greatest production for a given chamber-space, and the smallest consumption of nitre. We may say generally that the chamber-acid is kept much stronger in the majority of English works than in the majority of Continental works. Whilst the former mostly keep the acid in the leading chamber from 120° to 130° and the drips often 5° to 10° higher, the usual practice on the Continent is to keep it at 106° to 110°, or at most 116° Tw. At the Rhenania works the acid runs away from 106° to at most 116° Tw. In America I found from 112° to 116°. Only exceptionally higher strengths (up to 124° Tw.) are met with on the Continent or in America.

It is unnecessary to say that both English and Continental manufacturers firmly believe that they are in the right, the former in making stronger, the latter in making weaker chamber-acid. Both contend that in their, and *only* in their way, the best results are obtained. It is difficult, if not impossible, to arrive at any certain decision on that question from a comparison of the data supplied by various works as to the strength of acid, the yields, the consumption of nitre, the chamber-spaces, and so forth. This difficulty arises both from the complication of the various conditions, which interact upon one another, and from the very frequent inaccuracy and incompleteness of the obtainable figures. It is therefore with all reserve that I proceed to give my own opinion on this question (which differs from that given in the first edition of this work, vol. i. p. 346).

All *theories* of the vitriol-chamber process seem to point to the preference of the *weaker* rather than of the stronger acid. Hurter, in his dynamical theory (*J. Soc. Chem. Ind.*, 1882, p. 10), arrives at the result that the chamber-space is inversely proportional to the quantity of nitrogen compounds present, and to the amount of water present in the gaseous condition; in other words, that, other conditions being equal, the quantity of acid produced within a given chamber-space is larger when weaker acid is made than when strong acid is made. It is true that the evidence given for this in the paper just mentioned from the actual results of a number of chambers is very scanty, and certainly not sufficiently conclusive in itself; this was unavoidable, as only such works were quoted which did not possess Gay-Lussac and Glover towers. But, at all events, no contrary assertion can be based on that evidence.

The theory propounded by myself, and the very similar one of Sorel, both of which will be found at the close of this Chapter, also demand that, other conditions being equal, the sulphuric-acid-forming reaction is promoted by a larger amount of water, up to the limit where an excess of water would produce other, injurious, reactions.

Another point to be considered is this, that it is practically impossible to prevent the loss of some nitre, dissolved in the chamber-acid as nitrosulphuric acid, but that the tendency of the chamber-acid to retain nitre in this form rapidly increases with its strength. Theory would therefore demand keeping the acid weaker in order to lose less nitre. Whether this is so or not in practice can only be proved by bringing together a great many *reliable* data, the difficulty of doing which has been pointed out before. It is a fact that sometimes "pale" chambers are the consequence of giving too little steam (that is, keeping the acid too concentrated), and that this evil can be remedied by turning on full steam for a short time, which causes the chamber to become red again.

The practice of most Continental factories, including several German and Austrian works, at which all the processes are followed up in the laboratory with the greatest care, and which are generally admitted to work with the greatest perfection, is in accordance with the just-quoted theories, and comes to this: that the acid in the leading chamber, that is at the same time that which is withdrawn from the process for use or sale, should not exceed 113°, and is best kept at from 106° to 110° Tw. In this way the best yield and the smallest consumption of nitre are attained.

The usual and practically the only reasonable motive of English manufacturers for making their chamber-acid so much stronger is, of course, this, that they save the expense and trouble of concentrating the acid for use or sale. But there is little or nothing in this in the great majority of cases. For the manufacture of superphosphates, which requires an enormous quantity of sulphuric acid, and for which many acid-works are exclusively employed, the strength of 110° Tw. is quite sufficient. For decomposing salt for sale and for making rectified oil of vitriol, a higher strength is certainly required. But at every works provided with Glover towers (that is, at every properly equipped works, and actually in the great majority of existing factories) there is no difficulty whatever in bringing all the acid up to 140° Tw. without any expense, even when starting from chamber-acid at 110° Tw.; and this is done even without Glover towers (for further concentration in platinum stills) at many works by means of the waste heat of the pyrites-kilns.

Some years ago, P. W. Hofmann (*Ber.*, iii. p. 5), starting from the (erroneous) assumption that sulphurous acid in contact with nitric acid and sulphuric acid of, say, 100° Tw., produces much nitrous oxide, N_2O, proposed to diminish the steam in the first chamber (which in his case was only a "tambour" of 3500 cub. ft. capacity) to such an extent that acid of 140° Tw. should be formed; in this way the acid dissolves much nitre, and is run into the following large chamber, where it gets diluted and gives up the nitre. He asserted that he had thus effected a saving of 1 lb. nitre on 100 lb. of sulphur; but as his original consumption of nitre and the yield are not stated, and as, moreover, his chambers had no Gay-Lussac and Glover towers, that alleged saving cannot convey any proof of the utility of his proposal, upon which a vigorous controversy was carried on in the 21st volume of the *Chem. News* (pp. 132, 164, 189, 200, 224). It was then mostly overlooked that Hofmann's small "tambour" of 3500 cub. ft. capacity had very little in common with an ordinary English leading chamber of more than ten times that capacity. Apart from all other reasons, the undoubtedly much greater wear and tear of the chamber, when worked in the described way, would tell much less with a small "tambour" than with a large chamber. But, for the reasons above stated, Hofmann's process seems wrong in principle, and has not met with any success whatever on the Continent, where it was first tried.

In England later on (since 1889), probably without any reference to Hofmann's proposal of 1867, several works in Lancashire began to employ much stronger acid in the leading chamber, up to 140° Tw. It is, of course, out of the question to lose the nitre dissolved in such strong acid; none of it must be used without first passing through the Glover tower, and as it would become too strong therein, and would be incompletely denitrated, a little water is run through the tower at the same time. At one of the works visited by me it was stated that, with the very low chamber-space of 17 cub. ft. per lb. of sulphur, the excellent yield of 41½ cwt. of 96 per cent. salt-cake was obtained per ton of pyrites, with the very small consumption of 15 lb. nitre per ton of pyrites (=0·67 per cent.). These good results were ascribed, firstly, to an extraordinarily large Gay-Lussac space; secondly, to the above-mentioned procedure, by which an unusually large quantity of nitre was supposed to be kept circulating in the vitriol-chamber. It was not denied that there was more wear and tear of the chambers; but it was believed that this was no more than would be compensated by the saving in the process.

At the time of my visit to the above and a few other works, where the same method was followed, the process had not been sufficiently long in use to enable a correct judgment to be formed as to the yield and the consumption of nitre. Everybody knows that it requires many months to make sure of this, and to avoid being deceived by accidental gains and losses. But even taking it for granted that the above-quoted excellent results were really confirmed in the long run, I am very strongly disposed to place these results rather to the credit of the colossal Gay-Lussac towers existing at that factory, of a width of 14 ft. and a height of 60 ft., than to that of keeping the chamber-acid at the dangerous strength of 140° Tw. It is clear that the large quantity of nitre kept in solution in the strong acid of the leading chamber can contribute but very little to the work of oxidising sulphurous into sulphuric acid; its work can be done only whilst running down the Glover tower. But then the same object can be attained quite as well, while keeping the chamber-acid at a lower strength, by supplying the Glover tower with more nitre, either (once for all) in the shape of nitric acid, or (continuously afterwards) in that of nitrous vitriol from the Gay-Lussac tower; the inert stock of nitre at the bottom of the leading chamber is thus very largely reduced, and the confessedly much greater wear and tear of this chamber and of the Glover tower is thus avoided. From all indications it is also likely that less chamber-space will be required in this than in the former case.

It is difficult to say anything general as to the strength at which the *drips of the first chamber* ought to be kept. At one works we find the drip-acid only 2° or 3°, at others 15° or more above the bottom-acid; at others it is always weaker than the bottom-acid. Everything depends on the position of the drips; but so much is certain, that in the same plant the difference between the strength of the drip-acid and that of the bottom-acid is nearly constant, and that the attendant must manage his chambers accordingly. On the average, the drips, where they are taken from the inside, clear of the chamber-sides, show about 10° Tw. more than the bottom-acid; but this holds good only for the ordinary style of working, not for that described above, where the bottom-acid is kept at 140° Tw.; in this case the drips are not very much or not at all stronger; and where the drips are collected at the chamber-sides they are generally somewhat weaker than the bottom-acid.

We have seen above (p. 311) that the tension of aqueous vapour varies both with the temperature and with the strength of the acid; for instance, at 80° (near the chamber-side), acid of 114° Tw. has exactly the same vapour-tension as, at 95° (only 2½ in. within), acid of 128½° Tw. Sorel observed that the acids collected at various points of the same transverse section of the chamber really showed such differences of strength, and that, therefore, it may be said that they are all at an equilibrium of aqueous-vapour tension. This shows how useless it is to compare the drips of different sets of chambers, unless they are fixed in a precisely similar position to one another.

The strength of acid in the intermediate chambers, between the first and the back chamber, is always below that of the first chamber. The second chamber, in a set of three, has generally about 10° Tw. less than the first; but with acid of 140° Tw. in the first chamber the difference between this and the second may amount to twice as much. In a set of four or more chambers the strengths will naturally diminish more gradually.

The *last or "back" chamber* is kept at very different strengths, according to whether there is a Gay-Lussac tower connected with it or not. In the latter case the acid is never kept above 75°, and sometimes as low as 50° Tw., or even less than that. It is, in fact, difficult to keep the strength higher, as there is so little sulphur dioxide present in this case, and as there must not in the chamber be a large quantity of nitre, in order to avoid losing an enormous proportion of it. Thus there is but little acid made here, and it is correspondingly weak. But such weak acid, even at 75°, causes the formation of much nitric acid, which must act on the chamber-lead and is otherwise injurious. Hence with the old style of working without nitre-recovery apparatus, the last chamber was always a very weak link of the set.

In the presence of a Gay-Lussac tower there is no reason whatever for keeping the last chamber below 90° Tw., or even a few degrees above this. There is no formation of nitric acid to be apprehended in this case, and the gases will be better dried in preparation for the Gay-Lussac tower. The practice of some works to go down as low as 75° or 80° Tw. in the back chamber cannot be at all recommended.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 301) prefers placing the "drips" in the connecting-pipes between the chambers, and keeps them as nearly as possible at the following strengths:—drip from Glover tower to 1st chamber = 95° to 105°; from 1st to 2nd chamber = 130°; from 2nd to 3rd chamber = 122°; from 3rd to 4th chamber = 105°; from 4th to Gay-Lussac = 85°. If the drip from No. 1 to No. 2 chamber stands lower than 130°, the consumption of nitre is increased. [The drips in the connecting-pipes do not correctly indicate the work done in the chamber, as in consequence of the far greater cooling-action the formation of acid in these places must be abnormally large.]

Sorel gives the following directions for the strength of acid to be observed in a set of three chambers (degrees Baumé):—

	Inside drips.	Side drips.	Acid in chamber-bottom.
1st chamber	57-55° Bé. up to the middle. 56 second half.	51-54° ...	... 54·5-55°
2nd chamber	52-53°	42-43° first half. 45-47° 2nd „	... 48-48°·5
3rd chamber	52-53°	45-50° „ „	... 48·0-44°·5

We shall now describe *the injurious results of a wrong supply of water* (as steam or spray) to the chambers.

The first and most obvious result of giving *too much steam* is this, that the acid gets too weak. But this is of less importance than another drawback immediately following. If the lower oxides of nitrogen meet with an excess of oxygen (which is always present in the chambers) *and at the same time with an excess of water*, the following reactions take place:—

$$2NO + 3O + H_2O = 2NO_3H;$$
$$N_2O_3 + 2O + H_2O = 2NO_3H.$$

That is to say, they are converted into nitric acid, which, in the first instance, is a much less efficient carrier of oxygen than nitrous acid, and, secondly, is to a great extent dissolved in the bottom-acid; here it assists the acid-forming process very little, and, moreover, acts upon the lead. So long as the bottom-acid is pretty strong (say, up to 90°), it will not retain the nitric acid for a long time, but again gives it off as lower nitrogen oxides by the action of sulphur dioxide; but if the excessive supply of steam continues, it will soon keep the nitric acid back; and as the process is thereby disturbed, even the steam[1] which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid is thus again increased. If this state of matters has once set in, it is not always easily remedied. Cutting off the steam is not sufficient; much more nitre must be put in as well; and yet the bottom-acid only gradually gets up to its normal strength In the meantime the yield falls off, the consumption of nitr increases very much, and the action of the nitric acid on th chamber-lead does permanent damage. Thus it is apparen that an excess of steam does very much harm; and great car must be taken lest the strength of the acid should go dow below the proper amount. The chambers soon show when the have too much steam by becoming pale. A pale chamber ofte gets red again in an hour after the supply of steam has bee partially cut off.

An excess of steam has another injurious effect, which ca only be explained in detail when treating of the theory of the chamber-process, viz., the formation of nitrogen protoxide, or even of elementary nitrogen, whilst the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrogen protoxide nor nitrogen can be reoxidised to nitrogen-acids; they escape with the other gases, and thus cause a loss of nitre.

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[1] Whenever here, and in other places, we speak of "steam" in connec tion with the supply of chambers, water in the shape of spray or mist is als meant; it would be tedious to mention this in every instar

We will now consider the opposite case, viz., that *the chambers receive too little steam.* According to the theory of the vitriol-chamber process, to be developed later on, this must deteriorate the conditions for the formation of sulphuric acid, since the substance formed in an intermediate state, viz. nitrososulphuric acid, cannot then be entirely decomposed into sulphuric acid and nitrous acid. It will in this case be either separated in the solid state, as "chamber-crystals," or else it will dissolve in the bottom-acid. In actual practice it rarely happens that the deficiency of water is so great as to lead to the formation of solid chamber-crystals within the chambers; more frequently this happens in the connecting-pipes. But it is all the more general, nay, unavoidable, that some chamber-crystals (commonly called "nitre" in this case) dissolve in the bottom-acid. We shall see later on that a certain quantity of "nitre" *must* be present in properly working chambers; but if there is too little steam, this quantity will be largely increased, both by a deficiency of water in the acid mist floating about, which leaves a large quantity of nitrososulphuric acid undecomposed, and by the excessive concentration of the bottom-acid, which enables it to hold more "nitre" in solution. Thus the nitre will be removed from its proper sphere of action, viz., the atmosphere of the chamber, and SO_2 will escape oxidation. Where the chamber-acid is directly used, without first passing it through the Glover tower, this nitre will be finally lost. All this, of course, happens less easily where the bottom-acid is kept at a lower strength, as is usual on the Continent; there is in this case more time for repairing a temporary deficiency of steam, as indicated by testing the drips and bottom-acids for strength and nitre.

A deficiency of steam also acts in this way, that the acid by becoming too concentrated may to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144° Tw. (and this will very rarely happen, even with faulty managements, there is not much harm done. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam; in the case of smaller chambers (tambours) none at all. But this may be carried too far; and then, in spite of the dark-red appearance of the chambers, there is a bad yield of acid, because the water necessary for its formation is missing, and SO_2 and O go away uncombined. This occurs especially when the chamber shows a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are nothing like so serious as those arising from an excess of steam.

Hurter (*The Manufacture of Sulphuric Acid*, Liverpool, 1882, p. 16) gives the following rules for utilising the indication of the chamber-drips:—

1st. If the strength of the acid in the drips is *correct* but deficient in quantity, the chamber is short of nitre.

2nd. If the strength is *high* and the quantity not far short, the chamber is very rich in nitre; but if the quantity is short, it has too little steam.

3rd. If the strength is *low*, but the quantity full up, the chamber has too much steam. If, on the other hand, the strength is low and the quantity short, the chamber is very poor in nitre.

It is needless to say that the indications afforded by these rules would be sometimes very misleading, the conditions being too complicated, if they were not supplemented by direct observations of the amount of "nitre," the temperature, and the composition of the inlet- and outlet-gases, as shown below.

Stinville (Ger. P. 144084) produces in the lead-chambers a circulation of cooled acid, diluted to such an extent that its steam tension is sufficient to furnish the aqueous vapour required for the process. There are three chambers, *a*, *b*, *c*; the gases pass from the Glover tower into *a*, and leave *c* for the Gay-Lussac tower. The bottom-acid flows from *c* to *b*, from *b* to *a*, and from *a* into a cooler, where it is cooled down by means of a water-coil and also diluted by fresh water; in this state it is pumped back again into the chamber *c*.

Supply of Nitre.

It is quite evident that those ingredients from which sulphuric acid is ultimately formed, viz., sulphur dioxide, atmospheric oxygen, and water, must be supplied to the chambers in proportions varying within very narrow limits only, as any undue excess or deficiency of one of these will cause a corresponding waste. Sulphur dioxide being taken as the given quantity, the proportion of water supplied, is kept so that a very nearly constant concentration of the chamber-acid is obtained; and in like manner the supply of air is regulated by the draught in such a way that a certain necessary excess of oxygen, but no more than this, is found in the exit-gas. But the matter is different with that reagent which does not enter into the composition of the ultimate product, and only serves as an intermediary agent for combining SO_2, O, and H_2O, without (in theory) suffering any real change or loss at the end of the process. We now call such an agent a *catalyser* (see later on); this is, of course, the "nitre," by which expression we understand all the compounds of nitrogen which are concerned in the manufacture of sulphuric acid, at whatever stage of oxidation or combination they may exist at a certain moment.

It is almost self-evident that the acid-making process can be made more or less rapid by supplying more or less nitre, and that this finds expression in the greater or smaller space which the process requires. In fact, considerable variations may be made in the supply of nitre, according to whether the chamber-space is to be utilised as fully as possible or not; and up to a certain extent it may be said that the supply of nitre must change in an inverse proportion to the chamber-space present. But certain limits do exist here as well, both in an upper and in a lower direction. If there is too small a supply of nitre, the reactions become too sluggish and very disastrous consequences follow, which cannot be avoided by any amount of chamber-space; and if too much nitre is supplied, the temperature rises too much, the chamber-lead is acted upon, and part of the nitre escapes the process of recovery. We shall refer to this subject in detail later on.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or not. In the latter case care must be taken not to have too much nitre-gas in the last chamber; for everything issuing from it is a total loss. Therefore the last chamber but one is kept strongly yellow or red, in order to promote the acid-forming process, but the last chamber only faintly yellow.

The bottom-acid in that chamber, which is usually kept at 50° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This state of the last chamber is attained by giving it much steam; but it will be seen at once that in this chamber very little work can be done unless a very great loss of nitre is suffered; for only if the latter be present in large quantity, the oxidation of sulphurous acid goes on all through the chamber. Therefore one of these two things must be done: either a large quantity of nitre must be sacrificed in order to utilise the last chamber, or the last chamber is practically used only for recovering part of the nitre; thus actually a third or a fourth of the chamber-space is sacrificed, and so much less sulphur can be burnt in that set. For all that, the last chamber is not merely a costly, but also a very inefficient apparatus for recovering the nitre; even if used as such, very little below 10 per cent., mostly above 10 per cent., of nitre in proportion to the sulphur must be employed in order to get a good yield. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. We thus effect a saving of a fourth, up to a third, in chamber-space, at least one of two-thirds in nitre, and mostly also better yield, because up to the last an excess of nitrous gas is present, and no sulphurous acid can escape oxidation by it. In this way the escape of noxious vapours is also much more completely prevented. The construction of the nitre-recovery apparatus, and everything pertaining thereto, has been described in the 6th Chapter. Here we shall only describe the way of managing the chambers themselves in this case. Supposing the set to consist of three chambers (the reader will easily reduce this to any other proportion by analogy), the first chamber into which, in any case, both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, or cascades, or Glover towers, or steam-columns, will always have an excess of nitre-gas. In spite of this the characteristic colour of nitrogen peroxide will not be perceived in the first chamber, both because the sulphur dioxide, likewise present in excess, constantly reduces most of the NO_2 to colourless nitric oxide, and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognised. In the second chamber the atmosphere is already much clearer; and as also there is very much less sulphur dioxide present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphur dioxide present, that the mixture of gases in the second chamber will only show a more or less reddish-yellow.

In the third chamber, however (in a set of more chambers, in the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There should be very little sulphur dioxide remaining here; and before the gas issues out of the chamber into the Gay-Lussac tower the sulphur dioxide ought to be entirely removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will consist not only of colourless nitric oxide, but also of red nitrogen peroxide. This is proved by the last chamber showing a dark red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas observed in the "sight" of the pipe leading to the absorbing-tower the red or orange colour ought to be quite decided. Within the chamber the red ought to be not quite transparent, but dimmed by a mist of water.

The *colour of a chamber* can be observed by opening the manlids on the top or the clay plugs in its side, but in a much more convenient and accurate way by glass windows put in the sides of the chamber itself (as described, p. 701). As soon as the last chamber turns paler, the cause of this must be sought for. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong; and by comparing the other symptoms, especially the strength and the nitrosity of the drips and bottom-acids, the special cause of the fault must be got at. When the last chamber becomes quite pale, it is certain that a great loss is suffered by sulphur dioxide escaping from it; and the latter, on its way through the Gay-Lussac tower, will even denitrate the nitrous vitriol contained therein, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Everything must therefore be done to avert the turning pale of the last chamber.

Apart from the colour, the gradual diminution of sulphur dioxide and the increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than that by colour that it is not worth while to enter upon it in detail. A chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best Continental works regularly make only two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyse the chamber-gas between as well; nor is this necessary, since its colour gives a sufficient indication for the purpose in question.

As well as testing the *chamber-acid* for its strength, it is of great importance to test it also for its *nitrosity* (percentage of nitrogen acids); and this forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitrososulphuric acid) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially because a number of impurities interfere with the accuracy of the process. In practice, however, a simple and momentarily made *colorimetrical test* with ferrous sulphate is sufficient for the object in question, and we shall now describe this.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen are present. With more nitrogen oxides the ring becomes darker; with still more the whole ferrous sulphate solution assumes a deep brown or black colour. In this case effervescence readily sets in, the liquid getting hot, and the dissolved nitric oxide, with the black colour, being driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes of 5 in. height is once or, preferably, twice a day taken to the chambers, and the tubes filled up to about 4 in. with samples of the drip- and bottom-acids of each chamber; at the same time the strength of each sample is taken by the hydrometer, and written on the stand at the bottom of each tube. The acid-samples are then tested at any convenient place, by carefully pouring on to each about half an inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths marked below, and taking into account the colour of the chamber-gas observed through the windows, a tolerably good idea of the process going on in the chambers is obtained. This certainly should be completed by an estimation of the sulphur dioxide in the burner-gas and of oxygen in the escape-gas, and also by testing the nitrous vitriol, etc., as we shall see in the next Chapter.

Kolb (*Bull. Soc. Ind. Mulhouse*, 1872, p. 309) gives a few analyses of chamber-acids, confirming what has just been said. They refer to an old-fashioned set without Glover tower and with nitric-acid cascades.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Density . .	1·489	1·417	1·445	1·480	1·488	1·478	1·420	1·457
SO_4H_2 . .	59·1	51·6	54·9	58·1	58·6	58·2	51·4	56·0
N_2O_3 . .	0·023	...	0·04	0·023	0·010	0·02	0·170	0·03
N_2O_5 . .	0·000	...	0·02	0·000	0·000	trace	0·040	0·00
SO_2 . .	...	0·008	...	...	...	...	...	...

a, acid from the first or denitrating tambour where the sulphur dioxide of the burner-gas meets the acid of the last chamber and the Gay-Lussac tower; *b*, the same when the chambers were short of nitre; *c*, acid from the tambour where the fresh nitric acid ran over the "cascade" (excess of nitre); *d*, the same, short of nitre; *e*, acid of the "large chamber"; *f*, acid of the last chamber, normal process; *g*, the same, large excess of nitric acid—liquid green and nitrous; *h*, the same, normal process.

The following rules may be laid down for the *reactions on nitre which the various samples of acid from the chambers and drips ought to show.* Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first or leading-chamber* ought not to show any nitre whatever; if it does so, it is a strong indication that the supply may be shortened. (It must be borne in mind that a slight quantity of nitre, which can be discovered by finer tests, is nearly always present even in the first-chamber acid, but the above-described rough test ought to show none at all or very little.) But first it must be ascertained if, on the other hand, the *drip* of this chamber does not show any nitre; for in this case we must infer that there is *too little steam* in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Mostly this will be confirmed by both drip- and bottom-acid being too strong; and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough; in this case the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the acid of the first chamber smells, on the contrary, of sulphur dioxide; if this is the case to any appreciable extent, there is a deficiency of nitre in that chamber.

The *middle* chambers ought to show already a faint reaction of nitre in the bottom-acid and a stronger one in the drips; the *last* chamber, in any case, a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case as well a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen both if there is too much and if there is too little steam in this chamber: if the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre; if, however, there is too much steam present, that phenomenon will take place which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed and will dissolve in the bottom-acid. Both faults are easily avoided if the last chamber is not kept weaker than 90° nor stronger than 110° Tw.; but sometimes insufficient draught may cause these faults as well. If, on the contrary, the last chamber still appears red, and even the drips still show nitre, but the bottom-acid none, this is an indication which must be instantly met by increasing the supply of nitre; otherwise the chamber itself will soon become pale. If both indications coincide, viz., a pale chamber and a ceasing or weakening of the nitre in the drip, this might still be due to an excess of steam; but rarely will it be so, as anyhow that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Whether the draught is insufficient is most easily tested by estimating the oxygen in the escape-gas; whether it is too large, by estimating the sulphur dioxide in the burner-gas; but in the case of very leaky chambers, which properly ought to have been stopped already, air enters directly into them, as is proved by the oxygen coming out too high in the escape-gas. Where no gas-analyses are made, the formerly mentioned external indications for judging of the draught are taken into account; but these are far more deceptive than gas-analyses. When the draught is not large enough, the nitric oxide does not meet enough oxygen to be oxidised; it is colourless, and, owing to its insolubility in strong vitriol, is altogether lost. This will be recognised by the appearance of red vapours on the gas issuing out of the chimney, where the nitric oxide is oxidised by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. When there is too much air present, the nitrogen acids are carried away mechanically, and the chambers equally lose their colour; at the same time sulphur dioxide goes away, as it has not time to be oxidised.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or entering of air through chinks in the chambers and mechanical carrying away of gas, will frequently *react upon the burners*, since by the insufficient condensation of gas the draught from the burners towards the chambers is diminished. Then all the appearances will take place which are caused by very bad draught in the burners, especially incomplete burning and formation of scars, which, again, weakens the draught. In this case as much nitre as possible must be given, in order to force a better formation of sulphuric acid; and, if necessary, even the burner-charges must be diminished.

But if the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, it is due to want of the latter, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. Undoubtedly several circumstances often act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, instead of N_2O_3, only NO or even SO_2 get into the absorbing-tower, not only will the draught have to be increased, but more nitre will have to be given as well, in order to make up for the loss. Just in the same way, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot entirely retain it), not only will the draught have to be moderated, but more nitre will have to be introduced till everything is in order again.

An *excess of nitre* is detected by the colour of the chambers being too dark, by the strong nitrosity of the acids, and by the fact of the Gay-Lussac acid showing the presence of nitric acid, consequent upon an excess of N_2O_4 in the last chamber.

We thus see that, in nearly every case, when anything goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time; it is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work; and every factory ought to possess facilities for it. If this should not be the case to a sufficient extent, and if without danger to the chambers it is not possible to introduce as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state by easing them in this way.

At some of the best-conducted works it is not thought sufficient to judge of the supply of nitre by the colour of the chambers, the testing of the drips, and so forth, but a system is introduced of constantly checking the amount of nitrous vitriol supplied to the Glover towers, its strength, and the amount of fresh nitre or nitric acid introduced in comparison with the amount of sulphur burnt, in order to keep the quantity of nitre present in the chambers at as constant a figure as possible. As an example of the way in which this account can be kept, I give the following figures, taken from an actual day's work in a well-conducted Continental factory:—

	SET NO. I.	SET NO. II.
Pyrites charged, kl.	10812	10000
Containing sulphur, less quantity left in cinders	4993	4735
Nitrous vitriol used, kl.	10138	10268
Average strength, expressed in nitric acid 36° Bé.	4·86	4·37
Equivalent to acid of 36° Bé., kl.	493	449
Fresh nitric acid supplied, kl.	200	186
Total as nitric acid 36° Bé., kl.	693	635
Equivalent to 96 per cent. nitrate of soda, kl.	520	476
96 per cent. nitrate introduced for each 100 parts of sulphur burnt	10·4	10·1

This quantity, that is, about 10 parts of 96 per cent. nitrate to 100 of sulphur, may be considered a minimum, and only admissible where the chamber-space is very ample—say, about 24 cub. ft. per lb. of sulphur. With less chamber-space, much more nitre, equivalent to 15 or even 20 parts of 96 per cent. nitrate of soda to 100 sulphur burnt per diem, is put through the system. For the "high-pressure style" (v. p. 639, etc., etc.) up to 25 parts of nitre is used; but this involves a correspondingly large nitre-recovery apparatus, without which the waste of nitre would be very serious.

Pemberton (*J. Soc. Chem. Ind.*, 1883, p. 414) quotes a total supply of 15·6 parts of nitre passing through the chambers for every 100 parts of sulphur burnt in the shape of brimstone, with 19·2 cub. ft. per lb. of sulphur. In this case a Gay-Lussac tower was used; whilst in three other cases, where there was no Gay-Lussac, from 8 to 10 parts of nitre were consumed, but with 26·8 to 35·7 cub. ft. of chamber-space. As he gives no details as to yields, his figures possess very little value.

Benker (commun., 1902) employs as a rule 13 parts total $NaNO_3$ to 100 sulphur burnt in twenty-four hours. With very well constructed chambers (*cf.* his views on that point, p. 625) this quantity may be lowered to 9 or 10 parts, but with wider chambers it must be raised to 18 parts $NaNO_3$. This allows with "high-pressure work" to make 8 or 9 kl. acid of 116 Tw. per cb.m. of chamber-space (say, 0·3 to 0·37 lb. H_2SO_4 per cub. ft.). When starting a new set of chambers, the first care is to see that the above quantity of nitre is provided. (*Cf.* also the statements of Davis, p. 640.)

Proposals for Modifying the Ordinary Way of Supplying the Chambers with Nitre.

A proposal made by the Manufacture de Javel (B. P. 1752, of 1882) seems to be worthy of more notice than it has received. The nitre is not to be introduced into the leading chamber only, where the temperature may thereby become excessively high, but to a small extent also into the following chambers, whose temperature is sometimes too low. Even the acid for feeding the Gay-Lussac tower is to contain a little nitre, in which case no SO_2 can escape through the tower.

The United States Chemical Company, Camden, N.Y. (Amer. P. 325262, of 1885), injects nitrous vapours into the last chamber, after having first injected steam, in order to counteract any too strong reduction of the nitrogen-oxides.

Starting from a contrary view, Benker (B. P. 1168, of 1895; *cf.* Kienlen, *Monit. Scient.*, 1895, p. 311) injects SO_2 (in the shape of gases from the front of the first chamber) into the last chamber, in order to remedy the drawback, occurring in the "high-pressure work," that vapours of N_2O_4 are formed which, as he believes, are not sufficiently absorbed in the Gay-Lussac tower. These are to be reduced to N_2O_3 by SO_2. This is evidently the same principle as that involved in Benker's former process (p. 839); the only difference is that he injected the SO_2 immediately in front of the Gay-Lussac tower, and that Benker now sends it into the last chamber. In regular work this process might act injuriously; but in cases where there is an excess of N_2O_4 it may do good. According to a communication from the inventor (1902), this process is not applicable where there is a great distance between the first and the last chamber, in which case the SO_2 contained in the gases aspirated from the first chamber by means of the injector, is changed into H_2SO_4 in the connecting-tube.

The Swiss Société le Nitrogène (Fr. P. 404071) replaces nitric acid in the lead-chamber process by a mixture of nitroso-sulphuric acid and nitric acid, obtained by thoroughly saturating concentrated sulphuric acid, of 75 per cent. SO_3, with nitrous gases diluted with a great extent of air or an indifferent gas.

Temperature of the Vitriol-Chambers.

At every sulphuric-acid works the temperature of the chambers is a subject of constant observation on the part of the attendants, and it is generally understood that the regular and economical working of the process is intimately connected with keeping the temperature at a certain height, different in different parts of the same set of apparatus, and considerably varying in analogous parts of the apparatus at different works but to be kept as nearly as possible equal and constant in the same place. The care with which the observations of temperature are made certainly varies very much. In Germany for many years past *thermometers* have been fixed in several parts of the chambers, generally near the "drips" (p. 698), and their readings are regularly recorded. In France and particularly in England this has been very much less the case; even in large and otherwise very well-managed works chamber-thermometers were frequently not to be found even in recent times, and it was often thought sufficient to test the temperature of the chambers by putting the hand upon the lead. It is hardly necessary to say that the latter plan is decidedly faulty, and the small expense and trouble of applying and using thermometers ought never to be shunned.

This is independent of the question, whether a certain temperature is or is not the theoretically best for the process of sulphuric-acid making, and whether this is the *cause*, or the *effect*, of the economical working of the chambers; for there is no diversity of opinion as to the fact that all causes leading to a faulty process act either directly or indirectly on the temperature of the chambers, and that the observation of the latter is one of the most important guides for judging of the proper working of the acid-making process.

Considerable diversity of opinion exists concerning the *best temperature for the chamber-process*; but there is no doubt as regards some general facts. The temperature of every chamber diminishes from front to back, and naturally even more that of the last chambers compared with the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot that it cannot be touched by hand for any length of time, say 50° to 65° C.: in the absence of any cooling-apparatus, Glover tower, etc., the heat becomes so high that the lead cannot be touched with impunity; but in that case the chamber will not last very long. The second chamber mostly shows on the outside hardly more than blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60° C. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside its temperature varies from 40° to 30°, and below that.

At the Aussig works I noticed in September that the tambour showed 60°; the large chamber in its first part 45°, in its last part 43°; the first back chamber 30°, the last (kept without any steam) 20° C.

At Stolberg (1902) the maximum temperature in the front part of the first chamber was 70° to 80° C. in summer, and 10° or 15° less in winter.

At Oker, in 1891, during the cold season, the first chamber showed 70° in front, 60° in the back; the second chamber, front 50°, back 44°; the third chamber, front 35°, back 25°. During the summer season the temperatures are 10° to 15° higher in the front, 5° to 10° higher in the back part.

At Salindres the leading chamber is kept at an average of 65° in summer, of 55° in winter. This is a refutation to the assertion of Favre (*Monit. Scient.*, 1876, p. 272), according to whom in the south of France the chamber-process is already disturbed at 65°. But it is true that many skilled chamber-managers prefer working the leading chamber as nearly as possible at 50° to 60° only.

Dr Stahl informs me that in a set of three chambers for brimstone, working without a Glover tower, but where part of the heat of the burner-gas was employed for concentrating acid, the temperatures ranged as follows:—

In the first chamber, near the entrance of the gas, from 80° to 90° C., according to the outside temperature.

In the second (main) chamber, in the middle, from 50° to 60° C.

In the third chamber, about 10° C. above the outside temperature in summer, and 20° C. in winter.

The numerous observations communicated by Crowder (*J. Soc. Chem. Ind.*, 1891, p. 301) contain nothing of importance.

The opinion expressed by H. A. Smith, according to whom the best temperature would be nearer 100°, is not based on any valid reasons, and seems to be shared by very few practical men; on the contrary, such high temperatures are universally assumed to be extremely injurious to the chamber-lead, and are carefully avoided. In Europe, 90° or 95° is probably the maximum temperature employed anywhere; but in America I found in one place, where zinc-blende was burned, a temperature of 100°, and it was asserted that this chamber (of course, the first of the series) suffered less than the last; but they had only a few years' experience at that works, so that we cannot accept that statement as conclusive.

The *lower* limit of temperature is by Schwarzenberg put at 40° to 50° C., because otherwise there would not be a sufficient quantity of water remaining in the state of vapour; he asserts that in cool weather a set of chambers is less easily started than in warm weather, and that in winter more nitre is used than in summer. I must contradict this assertion of Schwarzenberg's, both from my own and from many other practical men's experience. Unless the temperature of the chambers sinks so low that ice is formed in them (which may happen in back chambers kept without steam), no excess of nitre is required in winter; on the contrary, at all well-managed factories known to me it is asserted that they regularly require less nitre in winter than in summer, and that the work altogether proceeds better in the cooler season.

We have also seen (p. 730) that it is a mistake to assume that the water exists principally in the state of vapour within the chambers.

A most remarkable case is presented at the Freiberg works, where the cooling of the burner-gas, in order to condense the arsenious acid, is carried on so far that the temperature is equal to that of the outer air, and in winter the gases often enter the chambers at 0°. In spite of this, no inconvenience is felt, and no special contrivances or precautions need be employed; the temperature within the first chamber soon rises to 60° and upwards.

On the other hand, it cannot be doubted that there is at all events an upper limit, beyond which the temperature of the chamber ought not to go. We have seen in Chapter III. (p. 346) that with the same gaseous mixture a comparatively slight rise of temperature, from 70° to 80°, is sufficient to convert the oxidation of NO to N_2O_3 into a reduction of N_2O_3 to NO. Unfortunately we do not yet know the conditions of the process to the extent necessary for *à priori* fixing the upper limit of the temperature of the chambers with any approach to certainty.

In normal circumstances the temperature of the first (leading) chamber will have a direct relation to the quantity of work put upon the system. Whilst with the ordinary allowance of 20 cub. ft. of chamber-space per lb. of sulphur the normal temperature is, as before stated, from 50° to 60°, or at most 65°, it is, with forced work (15 or 12 cub. ft. per lb. of sulphur), 80° at the inlet and rises to 90° or 95° further on; even at the outlet it is still 15° or 20° over the temperature of the ambient air.

Benker (communication, 1902) considers a difference of 10° C. between the inside and outside temperature in the last chamber as a mark of excellent work; 18° or 20° should be never exceeded. He regularly fixes a thermometer on the outside as well as one inside, a course much to be recommended.

The temperature of the chambers depends upon various causes. It is raised by the heat of the burner-gases, by that of the steam introduced, and (in a far greater ratio) by the chemical reactions of the acid-making process; sometimes in hot countries and in unprotected chambers, by the heat of the sun. Part of this heat is withdrawn by the radiation from the thin and quickly conducting leaden walls of the chamber, also by the heat contained in the escaping gas and in the acid drawn off. The loss of heat by radiation will vary according to the season, to the wind, etc., but, of course, much less with chambers enclosed in buildings than with those exposed to the weather. Since for a given time both this influence and the heat brought in by the burner-gases and withdrawn by the exit-gases and the acid manufactured vary but little, the inner temperature will practically be governed by the intensity of the chemical reactions.

The facts now stated prove by themselves that, as I have urged before, *frequent observations of the temperature of the chambers are of great importance for the proper management of the process.* Although the temperatures at the various parts of the apparatus show very great discrepancies at different works, they are almost constant in the same set of chambers, so long as everything is in good working order; and for this reason any considerable rise or fall of the chamber-thermometer, to the extent of say 5° C., is a certain sign that there is some irregularity which should be remedied. This indication is all the more valuable as it is instantly observed without requiring any tests or loss of time, and it is accessible to any ordinary working-man without the aid of a chemist.

One of the most systematic series of observations of the temperatures in different places of a set of chambers was made at the Uetikon works by Lunge and Naef (*Chem. Ind.*, 1884, p. 17). Three readings were made every day, and the following are the averages of a prolonged period, both for (A) moderate duty of chambers (4·4 tons pyrites for 129,000 cub. ft., or 29 cub. ft. per lb. of sulphur), and for (B) intense duty of chambers (6 tons pyrites, or 20·8 cub. ft. per lb. of sulphur). The strength of the acid in the "drips" fixed near the thermometers is also indicated. The extreme variations of the chamber-temperatures, of which only the averages are given here, did not exceed 3° or 4° C. The temperature of the outer air varied far more, viz., 3° to 17° in the fourteen days' working of A, and from 5° to 20° C. in the ten days' working of B; but this did not influence anything except the last chamber. The chambers had all the same width (28 ft. 4 in.) and height (23 ft.); but the leading chamber was 138 ft., the second 65½ ft., and the third 36 ft. long.

	A. Moderate duty.		B. Intense duty.	
	Temp. C.	Strength. Tw.	Temp. C.	Strength. Tw.
Pipe coming from Glover tower	65	...	75	...
Front of leading chamber, near bottom	60	123	69	123
Middle ,, near bottom	60	112½	71	116
,, ,, midway up	61·8	...	73	...
,, ,, near top	64·5	116	76	116
Pipe between first and second chamber	45	119½	57	...
Second chamber near bottom	32	116	41	116
Pipe between second and third chamber	27	...	35	119½
Third chamber	19	116	24	116
Outer air	9	...	12	...

This shows in the first chambers a difference of from 9° to 12° between moderate and intense duty of the chambers. The temperature was very distinctly influenced by the quantity of nitre: with strongly red chambers it was much higher in the front than in the back part; with paler chambers the difference was less, the reaction also going on more equally. At the top of the first chambers the gases were from 4° to 5° hotter than at the bottom, but gas-analysis showed that the gases were not richer in SO_2 and O in the former than in the latter case.

Further experiments were made on the cooling-influence of the radiation from the chamber-walls. The following are the averages of seven days' observations at distances of 10, 4, and 2 in. from the chamber-side, with an average outer temperature of 19°:—

	Distance from chamber-side.		
	10 in.	4 in.	2 in.
Pipe from Glover tower	78°	...	...
Front of leading chamber	72	71	69°
Middle ,, near bottom	74	73	70
,, ,, midway up	76	75	73
,, ,, near top	80	79	77
Second chamber	52	51	50
Third chamber	33	33	32

At an outer temperature of 19°, therefore, the cooling between 2 and 4 in. from the chamber-side averaged only 2°, between 4 and 10 in. only 1°. At lower outside temperatures of course the cooling action would be somewhat stronger. Greater differences were found when the following observations were made in the centre of the chamber by lowering a maximum thermometer by means of a wire through the chamber-top and reading off at the other places as before (the table gives the average of ten observations, at an average outside temperature of 18°):—

Pipe from the Glover tower	73°
Front of leading chamber	69
Middle of ditto, 10 in. from side, bottom	70
" " " " midway up	72
" " " " top	76
" " centre of chamber, bottom	75
" " " " midway up	78
" " " " top	80
Second chamber	50
Third chamber	29

This shows a difference of 5° between the centre and a place 10 in. from the sides, so that there would be 8° between the centre and the sides. This would seem to indicate that the hot current of gases moves less quickly in the centre than near the sides, and it agrees with the fact that the percentage of SO_2 and O in the centre is greater; that is, that the reaction is less advanced there than near the sides in the same transverse section of the chamber. This would agree both with the theory of Abraham (to be mentioned further on), according to which the gases move in a spiral course from the front to the back end of the chamber, and with that of Sorel, as we shall see in Chapter IX.

The preceding observations clearly show that the chemical reactions produce a rise of the temperatures, as the heat of the gases in the middle of the leading chamber near the top exceeds even that of the gases arriving in the Glover tower, in spite of the cooling action of the air traversing a distance of 70 ft. from the front to the place of observation. This is confirmed by special observations in the fore part of the chamber, where the formation of acid is most energetic:—

	Bottom.	Midway.	Top.
33 ft. from front end	80·5°	83°	81°
66 " " "	75	78	80

Special interest is also afforded by observations made to ascertain the effect of using either *steam* or a *spray of liquid water* for feeding the chambers.

	Steam. (Outer temp. 12°.)	Water-spray. (Outer temp. 24°.)
	°C.	°C.
Pipe from Glover tower	69	73
Leading chamber, bottom	71	73
,, ,, midway	73	75
,, ,, top	76	78
Pipe from first to second chamber	57	68
Second chamber	41	53
Pipe from second to third chamber	36	47
Third chamber	24	31

It is true that in the second case (water-spray) the outer temperature was 12° higher than when using steam; but we have seen above that this influences especially the first chambers but little, and we may thence conclude that there is no sensible difference in temperature between the application of water as steam or that as liquid spray. All this confirms the paramount influence of the chemical reactions.

The following diagrams, Figs. 333 to 337, show the just-mentioned results graphically, the length of the chambers being approximately represented. In Fig. 333 the thick line represents the temperature-curve for a normal duty (20·8 cub. ft. chamber-space), at 12° C. outer temperature; the dotted line for moderate duty (29 cub. ft.), at 9° C. outside; the upper faint line the temperatures observed with a liquid water-spray at 24° outside. Fig. 334 gives the temperatures, obtained in the same series of experiments, as observed in the same transverse section near the bottom, midway, and near the top (the lines have the same meaning as in the preceding figure). Fig. 335 shows the temperature-curves in the longitudinal section of the chambers; the dotted line representing the observations taken at midway height, the thin line the bottom, and the thick line the top. They show very clearly how the temperature is raised by the chemical reactions; near the bottom and at a midway height it begins to fall in the second quarter of the leading chamber, but at the top it keeps up as far as midway. Fig. 336 shows the temperature at different heights in the centre of the first chamber; the dotted line at a distance of 33 ft., the thick line at 66 ft. from the front end. Fig. 337 shows the increase of temperature from the outside towards the inside (cooling action of the walls.

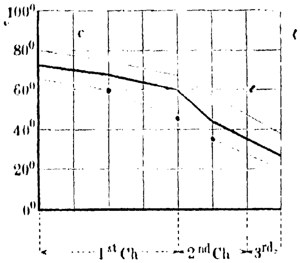

FIG. 333.

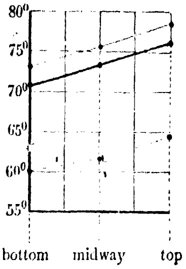

FIG. 334.

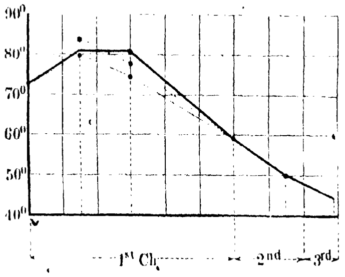

FIG. 335.

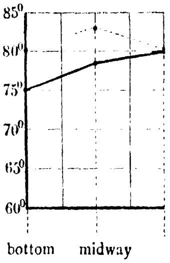

FIG. 336.

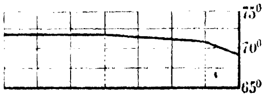

FIG. 337.

Eschellmann (*J. Soc. Chem. Ind.* 1884, p. 135) has examined numerically the relative influence of steam and nitre on the temperature of the chambers. The following is a summary of his investigation. Taking the drips in the first chamber = 130° Tw., this corresponds to the compound H_2SO_4, $2H_2O$ (molecule = 134), or to an evolution of 53480 + 9418 = 62898 cal. for 134 g. of that acid. The 54 g. of steam, at 125° C., required for forming H_2SO_4, $2H_2O$, represent 34809 cal. We will now assume that more steam is introduced, and we will put an extreme case, viz., the formation of $H_2SO_4, 3H_2O$. This means another 18 g. steam of 125° = 11603; whilst by the reaction $H_2SO_4, 2H_2O + H_2O$, 1729 cal. are evolved. We must, however, deduct the heat corresponding to a chamber-temperature of 50° = 50·087 cal. per gramme of water, which is left in the product, and we thus arrive at the following figures:—

The formation of:

$H_2SO_4, 2H_2O$ evolves 62898 + 32105 = 95003 cal.
$H_2SO_4, 3H_2O$ „ 95003 + 10702 + 1729 107434 cal.

Taking the gas entering the chambers to contain 6 vols. SO_2 in 100, this means introducing in the first case 3 × 6 vols. H_2O, and increasing the total to 118 vols.; in the second case 4 × 6 vols. of water, or a total of 124 vols. Thus we have—

For 118 vols. an evolution of 95003 cals. : 1 vol. 805.
„ 124 „ „ 107434 „ : 1 „ 867.

Now taking the chamber-temperature at 50°, the outer air at 15, the difference of 35 must be produced by the above reactions. The proportion 805 : 867 : : 35 : 37·6 shows us that introducing so much more steam that the quantity of water in the sulphuric acid is increased by a whole molecule (and thus bringing down the drips from 130° to 110° Tw.) makes a difference of only 2·6 C. in the chamber-temperature. The maximum variation produced by changes of the outside temperature, even in summer, when they are greatest, were not found to exceed 5° C. On the other hand, the following observations were made concerning the influence of the *nitre* on the chamber-temperature. Two sets of chambers, burning about equal quantities of pyrites, were supplied with their nitre exclusively by means of nitrous acid from Gay-Lussac towers, and therefore in a continuous fashion, while all the potting of fresh nitre was done in a third, larger, set of chambers, at intervals of two hours. Now the two small sets show no variation of temperature except what is due to the variation of the surrounding air, namely, between 50° and 53° C.; but the large set shows a regular variation from 48° to 68° C., the lowest temperature occurring immediately before potting, when the first chamber is least supplied with nitre, and slowly rising after the potting of fresh nitre. The thermometers were inserted at a distance of 22 ft. from the gas-inlets; the temperature of the gas entering was 35° C. The difference between the small, continuously supplied sets, and the large, intermittently supplied set, so far as temperature is concerned, cannot be ascribed to any other cause than the continuous or intermittent supply of nitre. This was conclusively proved by a special experiment in which one potting was missed, so that the only supply of nitre to that set came from a small quantity of nitrous vitriol running down the Glover tower, amounting to but 20 per cent. of the regular supply. In this case the temperature of the gases, entering at 35°, rose only to 41°, the strength of acid at the drips fell rapidly, a large escape of sulphur dioxide took place at the Gay-Lussac tower, and the chambers worked very irregularly, until not only the missed nitre was put in, but an additional quantity required to compensate for the nitre lost by reduction to nitrous oxide. Eschellmann's experiments are a strong argument in favour of the Continental plan of feeding the chambers with nitric acid.

Sorel (*Z. angew. Chem.*, 1889, p. 271) found that the difference of temperature between the front and back end of the first chamber, measured 5 ft. above the bottom, is only 2°, which is accounted for by the fact that the heat produced by the chemical reactions is only slowly abstracted from the gases by radiation from the walls. The space close to the lead walls is, of course, coolest (*cf.* Fig. 337, p. 944); from here towards the interior of the chamber the temperature increases quickly, and in many cases reaches a maximum at a distance of from 4 to 6 in. from the wall; after this it first sinks and then generally rises again towards the centre. Unfortunately, not many observations were made; but we will quote that series which is fullest (the temperatures, as remarked by Sorel himself, were extremely high, the season being very hot):—

Close to the lead	78°·5 to 79°·7
At 2 cm. distance	84
" 4 " "	91
" 6 " "	95·25
" 8 " "	95·25
" 10 " "	98·3
" 12 " "	97·3

Sorel believes that this difference of temperature is strong evidence in favour of Abraham's theory of the path taken by the gases within the chamber (see below); he also makes a most important use of it in his own theory of the formation of sulphuric acid (*cf.* below).

We must also mention an *abnormal state of things* which is sometimes observed, namely, a rapid sinking of the temperature of the first chamber, whilst that of the last chamber rises far above the proper degree. This is always accompanied by the colour of the gases getting paler, first in front, then also behind, so that even the last chamber may become quite grey. At the same time there is a great deal of liquid condensing on the glass of the "sights." Ultimately the quantity of sulphur dioxide going away unoxidised may become so large that the nitrous vitriol within the Gay-Lussac tower is denitrated, and the nitric oxide escaping, on contact with the air outside, forms dense red clouds. This state of things is brought about by all the causes which disturb the proper process—want of water, want or excess of steam or of air: all of these tend to keep the process back, so that the first chamber does too little, and the last chamber too much work. An examination of the composition of the gases at the inlet and at the outlet, as well as of the strength and nitrosity of the drips, will lead to localising the cause of the disaster and admit of applying the proper remedy. Usually, together with all other remedies, a fresh supply of nitre must be given, in order to get up the temperature of the first, and reduce that of the last chamber; that is, to bring back the maximum of production to its proper place in front of the apparatus. Where it is impossible to get enough fresh nitre into the chambers, the pyrites-burners must be kept back, to diminish the amount of sulphide dioxide in the chamber atmosphere. At all events, the indications of the thermometer in the *last* chamber are very important; if it rises above the normal point, the proportion of sulphur dioxide to that of the nitrous gases and steam is sure to be wrong, and should be remedied at once before more mischief is done.

Cooling the Chambers.—Pratt (Amer. P. 715142, 2nd December 1902) cools the chambers, towers, flues, or conduits by a cooling medium without bringing them directly into contact with the latter; also the hot uncombined gases, which are then passed again into the chamber.

Lagache (Ger. P. 144084; Fr. P. 350363) cools the gases from the hottest part of the chambers, especially for the "high-pressure style," by taking them out by means of a fan, passing them through a cooler and then back into the chamber.

Depth of Acid.

It is a general belief among practical men that the *depth of acid at the bottom of the chamber* influences the completeness and regularity of the chamber-process. In their opinion the best yield and the most regular work is only obtained by keeping a good stock of acid in the chambers, say 9 in. or more. On the contrary, a very experienced acid-maker, M. Delplace, emphatically denies that the process is improved by a great depth of acid. He was in a position to start a chamber (whose sides were burnt to the bottom) without any acid at all: the drops could be heard to splash upon the lead as they fell down; yet both the yield of acid and the consumption of nitre (1 part to 100 rectified O.V.) were as favourable as in any other case. It must not be overlooked that a very great depth of acid diminishes the available chamber-space.

I for my part am inclined to favour the view that it is of great importance for the regularity of the chamber work to keep a somewhat deep layer of acid at the bottom of the chambers. The probable cause of this is the fact that this layer serves as regulator for the variations of strength and the percentage of nitre in the acid directly connected therewith. This view is completely confirmed by observations communicated to the 30*th Alkali Report*, p. 66, by Mr R. Forbes Carpenter. At a factory where the chamber received its nitre mostly in the shape of waste acid from the manufacture of nitro-toluol, a film of nitro-toluol was formed on the surface of the chamber-acid, and this shutting-off of the acid from the atmosphere of the chamber caused exactly the same irregularity in the working of the chamber as a low depth of the acid would do. The acid at the bottom no doubt mainly serves as regulator for the nitre.

My opinion in this respect is altogether shared at Stolberg (1902).

The *removal of the sulphuric acid formed* in the chambers, which to a great extent is not lying at the bottom, but is carried on by the gases in the form of mist, is effected by

Cellarius (Ger. P. 166745) by introducing steam during the passage of the gases from one chamber to another in such manner as to create a centrifugal action and a whirling motion, in a lead tower packed with coke which causes an intimate mixture of the gases and the separation of the sulphuric acid in the form of drops. This is practically the same process as goes on in all "reaction towers" of which we have spoken *suprà*, pp. 656 *et seq.* An additional patent (Ger. P. 183097) of the same inventor employs for the same purpose, in lieu of coke, two concentric perforated cylinders, with a number of perforated partitions in the annular space between the cylinders; through which the gas is forced to pass by means of a turbine; thus the mist of sulphuric acid and the sludge are precipitated without the necessity of employing steam for this purpose.

General Remarks.

In checking the process it must never be overlooked that the same symptom may be owing to various causes. Thus the acid may get weaker either by a falling-off in the make or by an excess of steam. The draught may be lowered either by a smaller acid-production, or by atmospheric influences, or by the gas-flues getting stopped up with deposit. An insufficient conversion of sulphur dioxide into sulphuric acid may be caused by too weak or too strong a draught. The nitre may decrease in the chamber both through an excess of steam, which leads to formation of nitric acid, and through a deficiency of it, leading to chamber-crystals getting dissolved in the bottom-acid; and in both cases the strength of the vitriol falls off. Owing to the fact that in acid-making a certain effect may be caused by different circumstances, the management of chambers is not an easy task, but requires great judgment and experience.

Irregular Working. Loss of Nitre.

Having so far stated the conditions of the *normal* vitriol-chamber process, we must also consider how the process may become *anomalous*, that is *faulty*, which must in every case lead to losses both of nitre and of sulphur compounds.

Sometimes "free" *nitrogen peroxide* appears in the last chamber (never before). It has been proved by Lunge and

Naef (*Chem. Ind.*, 1884, p. 8) that this happens when the supply of nitre is abnormally strong, irrespective of a larger or smaller excess of oxygen, of which there is always far more than enough present. In this case the formation of sulphuric acid is finished before the proper time; there is next to no SO_2 in the last chamber, and the nitrous anhydride, which cannot be again taken up by the chamber-gases, is altogether dissociated into NO and NO_2, the former being equally oxidised to NO_2. The latter where it touches the chamber-acid dissolves in it and forms both nitrous vitriol and nitric acid. Most of the NO_2, however, passes into the Gay-Lussac tower; and as the size of this apparatus is only calculated to meet normal requirements, it cannot retain all the nitrous vapours, but emits a good deal of it into the air in the shape of ruddy vapours, thus causing a corresponding loss of nitre.

Far more serious are the consequences of a *lack of nitre*. In this case the formation of sulphuric acid is too slow, and there is too much SO_2 in the back part of the chambers, thus causing a denitration of SO_5NH in the *wrong* place. Very much NO is formed, the chambers turn pale yellow, or, in extreme cases, grey, and the temperature is either too high or too low for proper working. Owing to the relative excess of water the formation of the intermediate compound SO_5NH is greatly impaired; and the NO now forms with oxygen and water nitric acid, which sinks down to the bottom and dissolves unchanged in the chamber-acid, and is thus withdrawn from the chamber-process. Such acid will not "show nitre" in the sense used by practical men—that is, it does not give out orange vapours on addition of water, because it contains little SO_5NH, but for all that it may contain so much nitric acid that the chamber-lead is seriously attacked. The nitric oxide, on passing into the Gay-Lussac tower, is not absorbed at all by the sulphuric acid, the excess of inert nitrogen preventing its action with SO_2 and O, and at the top both NO and SO_2 escape, thus causing a double loss. A third source of loss is the formation of nitrogen protoxide, N_2O, for which the conditions now exist to a much greater extent than normally (see below). All this leads to a bad yield of sulphuric acid from the first and to a great loss of nitre, and as this instantly reacts upon the chamber-process, the floating quantity of oxygen-carriers being diminished at a progressive rate, it is no matter of surprise that things get from bad to worse. Every practical man knows, and Eschellmann has proved it in detail (*J. Soc. Chem. Ind.*, 1884, p. 136), that when there has been lack of nitre from any cause whatever it is necessary to introduce *several times* the amount originally wanting or "saved," in order to remedy the "disease" of the chambers, as some people call it.

Causes of the Loss of Nitre.—It is notorious that in no case whatever is the recovery of the nitrogen oxides, employed in the manufacture of sulphuric acid, complete. Even with the best nitre-recovery and denitrating apparatus, and under the best possible management, the loss is never below 2 parts of $NaNO_3$ to 100 of sulphur burnt, and it is nearly always higher than that, 3 parts of $NaNO_3$ probably indicating the ordinary present average. The sources of this loss of nitre are various, and may be distinguished as mechanical and chemical losses. *Mechanical losses* are those caused by incomplete absorption of N_2O_3 or N_2O_4 in the Gay-Lussac tower, by the nitrous acid contained in small quantities in nearly every description of sulphuric acid withdrawn from the process for sale or use, and by any accidental leakages from working-doors, chambers, etc. *Chemical losses* are those caused by the reduction of the nitrogen oxides below the point where they can be reoxidised or absorbed in the Gay-Lussac tower. Generally this chemical loss is ascribed to a reduction to the state of nitrogen protoxide, or even elementary nitrogen, or (by Raschig) to that of ammonia; but the latter, according to Raschig's own statement, is found only in quite exceptional circumstances and need not be taken into account for ordinary purposes. That a reduction to N_2O does take place under certain conditions (excess of SO_2 and undue local excess of water) has been proved by R. Weber and by myself (p. 336); and it is likely that to a certain extent such conditions do obtain in every vitriol-chamber, but less than anywhere else just in the Glover tower, where such loss was at one time believed to take place (p. 854). Up to the investigation by Inglis (to be mentioned below), it was, however, entirely uncertain what proportion the mechanical and chemical losses bear to each other. The most extraordinary discrepancies exist in this respect. Some chemists asserted that the mechanical loss, more especially that caused by incomplete action of the Gay-Lussac tower, is by far the most potent source of loss of nitre (Lunge and Naef, *Chem. Ind.*, 1884, p. 11; Benker; Sorel, *Z. angew. Chem.*, 1889, p. 279); others were of the contrary opinion. It seems useless to go into the detail of this controversy here, as no conclusive proof was given either way, and we will only quote some of the other papers bearing on this question: Hurter, Davis, Jackson, Mactear, Cox, and Lunge, in vol. xxxix. of the *Chem. News* (pp. 170, 193, 205, 215, 227, 232, 237, 249); Eschellmann (*J. Soc. Chem. Ind.*, 1884, p. 134); Hamburger (*ibid.*, 1889, p. 167). An important part in the loss of nitre is caused by the *coke-packing* of the Gay-Lussac towers. I had long ago (*cf.* p. 791) proved that the coke reduces any nitric acid getting into the Gay-Lussac acid in the shape of N_2O_4, so that the nitrous vitriol issuing at the bottom contains only N_2O_3. I have shown (in the same place) that nitrososulphuric acid itself is reduced by coke, NO escaping. This action is greatly increased by a higher temperature, and this may be one of the reasons why it is expedient to cool both the gases and the absorbing acid as much as possible; it also seems to favour the use of Gay-Lussac towers containing a non-reducing packing (p. 792).

Concerning the formation of *nitrogen protoxide* (*nitrous oxide*), we have seen in Chapter III. (p. 336) that this will happen if NO (or N_2O_3) meets an excess of SO_2 *in the presence of water* or of very dilute sulphuric acid. The reduction may then take place according to the equation—

$$SO_2 + 2NO + H_2O = H_2SO_4 + N_2O.$$

It is not impossible that, under specially unfavourable circumstances, the reduction may even proceed as far as the formation of elementary nitrogen or of ammonia, but this evidently happens only quite exceptionally and to an altogether insignificant extent; whilst most chemists assume the formation of N_2O to occur to a small extent, even in normally working-chambers, at the places where locally water and sulphur dioxide are in excess. Actual proof of this, by showing the presence of N_2O in chamber-gases, formerly could not be given; in fact, the analytical methods so far at our command would hardly permit this.

All the more important is the work done by Inglis (*J. Soc. Chem. Ind.*, 1904, pp. 643 *et seq.*), who, at the suggestion of Ramsay, proceeded by the fractional distillation of liquefied chamber-acid gases, cooled to about 185 by means of liquid air. By this means, and by repeated rectifications at suitable temperatures, the substances present could be divided into the following fractions: (1) nitrogen and nitric oxide; (2) nitrogen protoxide and carbon dioxide; (3) sulphur dioxide; (4) nitrogen peroxide and sulphuric acid. The fractions were measured and then analysed in the ordinary way. The flue gases at the Silvertown factory were tested in this way, altogether 284 l. being treated with fairly constant results. An extremely small quantity of nitrogen protoxide was found, about 0·002 per cent. The conclusion reached from this is: that the "chemical loss" of nitre is negligible in so far as nitrogen protoxide is concerned. The gases contained about 0·04 per cent. nitric oxide, and about 0·03 per cent. nitrogen peroxide. The total loss of nitre being 0·1 per cent., 70 per cent. of this loss is accounted for by the mechanical loss in the shape of NO and NO_2, and depends upon the efficiency of the Gay-Lussac tower.

In the discussion following the reading of that paper, all the speakers agreed that the "chemical loss" of nitre in the ordinary working of the chambers was altogether insignificant. Divers especially pointed out that it is now unnecessary to assume the formation of the hypothetic compounds, suggested by Raschig (*cf.* p. 337).

Later on Inglis (*J. Soc. Chem. Ind.*, 1906, p. 149) describes very careful experiments made by his methods with flue-gases at a factory, which led to the same result, viz., that only very small quantities of NO_2 and N_2O_3 are reduced to N_2O in the chambers; about 50 per cent. of the total loss of nitre is owing to incomplete absorption of NO_2 and N_2O_3 in the Gay-Lussac tower, and Lunge's view in that respect is the correct one. In his concluding paper (*ibid.*, 1907, p. 670) he sums up his results as follows: (1) the amount of nitre lost as N_2O is less than 10 per cent. of the whole loss; (2) a considerable proportion is lost as nitrogen peroxide and nitric oxide, the relative proportions of these two substances depending upon the escape of SO_2; (3) there is a possible reduction to nitrogen.

It is a fact that, by enlarging the Gay-Lussac towers beyond the size formerly used, the loss of nitre can be greatly reduced, and mention of this has been made before (p. 786). But it would seem as if the practical limit in that respect had been already reached when the Gay-Lussac towers, with ordinary coke-packing, have a capacity of 2, or at most of 3, per cent. of the chamber-space. Any further addition of absorbing-power causes but an insignificant diminution of the loss of nitre. The cause of this is no doubt that pointed out by Bailey (*J. Soc. Chem. Ind.*, 1887, p. 92), that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit-gases with oxygen and nitrogen, and that therefore a complete absorption of N_2O_3 is an impossibility; Sorel (in the place quoted above) proves a similar reasoning by observation and calculation, showing that, in a special instance, the exit-gases were bound to carry away nitrous acid equivalent to 3·09 per cent. of $NaNO_3$ to 100 of sulphur—that is, more than the best working factories consume altogether, and my observations have accumulated convincing material for such conclusions. It is true that direct analysis of the exit-gases in many instances fail to account for more than a portion (say a third or even a quarter) of the nitre lost; but it cannot be denied that this may simply be an unavoidable fault of the analytical methods used, as it is extremely difficult, or rather impossible, to retain in absorption-tubes all the N_2O_3 or N_2O_4 diluted with ten thousand times its volume or more of other gases. Any reasoning based on the analysis of exit-gases is therefore extremely unsafe, if it intends to prove that the loss from that source is too small to dispense with the necessity of assuming a considerable chemical loss.

It is even more difficult to estimate NO in excess over the proportion $NO+NO_2$ when mixed with a very large excess of other gases, and hence the above-mentioned conclusions are all the more uncertain. The loss of NO may be reckoned partly among the mechanical and partly among the chemical losses. The former is the case when any NO which has come from the chambers themselves has only mechanically escaped oxidation into NO_2 and consequent absorption in the Gay-Lussac tower; but it must be reckoned as chemical loss if the NO has been formed within the Gay-Lussac tower itself by some reducing action on nitrous vitriol. We have seen that such an action may take place by an accidental excess of SO_2; but this happens only exceptionally, although it is possible that the SO_2 always present in exit-gases even with the very best work, in spite of its very slight quantity exerts a certain reducing-action in the Gay-Lussac tower. Hjelt (*Dingl. polyt. J.*, ccxxvi. p. 174; *cf.* also our first edition, p. 570) ascribed a certain loss of nitre to the oxidation of *arsenious* to arsenic acid in the Gay-Lussac tower, amounting to 0·12 nitre per 100 of H_2SO_4 made, and Davis (*Chem. News*, xxxvii. p. 155) went even much further in that respect; but the latter did not uphold his views later on, and even Hjelt's observation seems to have been quite exceptional, to judge from observations communicated to me in a letter from Dr Th. Ernst, of Lehrte. Evidently arsenious acid can play but a very small part indeed in that matter.

Distribution of Gases and Rate of Formation in the Various Parts of the Vitriol-Chambers.

The following observations and considerations possess far more than a merely theoretical interest. They are intimately connected with the questions — which is the best shape for vitriol-chambers? are contact-surfaces for the better condensation of the acid to be provided, in addition to mere chamber-space? what is the real duty performed by the various parts of a set of vitriol-chambers, and can that duty be performed in a more advantageous way? and so forth. These questions have been treated at considerable length in preceding chapters, and they also influence the theory of the Sulphuric Acid Manufacture (see below).

The experiments made by H. A. Smith, and recorded in his pamphlet, *On the Chemistry of the Sulphuric Acid Manufacture* (London, 1873; cf. *suprà*, p. 454), are entirely untrustworthy, as pointed out several times before, in more detail, in the first edition of this work, pp. 285 *et seq.* His conclusion, that the chief portion of the acid made in the chambers is produced and condensed close to the surface of the acid already formed in the chambers, has not been confirmed by any other observer, and we will not detain ourselves any further with it, as it is also in direct contradiction to his own analyses of the gases. Hasenclever (A. W. Hofmann's *Report on the Vienna Exhibition*, vol. i. p. 178) fixed lead dishes in several parts of his chambers, covering them over at a distance of a foot, and thus found that about the same quantity of acid was formed all over the chamber. His conclusion certainly cannot be proved definitely in this way, since the dishes act as contact-surfaces, as we shall see just now.

Mactear (*J. Soc. Chem. Ind.*, 1884, p. 224) has published an extensive series of observations on the distribution and condensation of the gases in the vitriol-chambers. So far as they go towards settling the point at which part of the chamber the principal formation of the acid takes place, they are of no use to us, as they were based on a wrong principle, viz., that of observing the quantity of acid condensed on trays of a certain surface. It has been frequently shown, and that by Mactear himself in the same paper, that solid (or liquid) surfaces within the chambers have an intense condensing action upon the acid, which means that the mist of impalpably small drops on striking such surfaces condenses into large drops and collects upon the trays; hence the quantity of acid running away from the trays is not that made in the space above them, but represents a very much larger quantity, made partly, and possibly to the greatest extent, at some distance from the place where the tray is located.

How unreliable is the plan of testing the amount of sulphuric acid formed in a special part of the chamber by means of collecting-trays has been very clearly shown by Naef (*Chem. Ind.*, 1885, p. 287). The condition supposed to exist by previous observers is this, that the trays collect all the acid formed in the vertical space above them. If it were so, next to no acid would be found when the tray is provided with a cover. If, however, the drops fall down in a slanting direction, some acid will be found, and its quantity ought to vary in proportion to the distance between the tray and the cover. But even this is not the case. Naef placed within the chamber on one side an open tray, and on the other side a tray with a wider cover suspended over it at a variable distance. The result of weekly averages was this:—that the tray with the cover 12 in. above it collected exactly as much as the open one, and even when the cover was only 4 in above the tray the acid collected was nearly as much as on the open tray. Repeated observations confirmed this result entirely. This surprising phenomenon cannot be explained by a slanting fall of the drops, for it would suppose the fall to take place at an angle of 20°, which cannot be produced even by the most violent movement within the chamber, far above anything which really exists. There is no other explanation than one to which a very large number of former observations in all possible cases, also those of Mactear, irresistibly lead—that the sulphuric acid, when formed, exists in the shape of a very fine mist which is very slowly deposited in the form of a rain of real drops, and is carried forward by the gases for long distances, but is suddenly condensed to real drops when striking against solid [or, perhaps, liquid] surfaces. Therefore the acid is not deposited at all in a liquid state where it is formed, but further on, in very different quantities according to the surfaces it meets; hence the apparent contradictions between the results of gas-analyses and those of measuring the acid condensed on trays. The latter mode of observation is utterly worthless for deciding the question of the progress of the chemical reactions; this progress must undoubtedly be studied by gas-analyses. This last method presupposes that the gases in any special transverse section of the chamber are somewhat, although not absolutely, equally mixed; but that this is so, has been proved by the results of Lunge and Naef (see later on) as well as by those of Mactear himself. The fact that nearly as much liquid acid is condensed on the trays near the top as upon those near the bottom of the chamber is easily explained by Abraham's theory of a spiral movement of the gases (see below), of which it is, indeed, a necessary consequence.

Hence we cannot accept Mactear's conclusion that the principal part of the acid is made in the upper portion of the chamber. In fact this does not agree with his own analyses of the chamber-gases, and even less with his further conclusion (p. 228 of his paper) that the principal condition is that of "having ample chamber-space, the form of the chamber not being so material." The argument that the sulphuric acid forming and falling rapidly towards the bottom of the chambers must displace the gases and force them to the upper portion is fallacious; for the volume of the acid forming is several hundred times less than that of the gases concerned in its formation, so that the above-mentioned action must be imperceptibly small.

Mactear's observations on the rate at which the acid is formed in different chambers of a set are very interesting. The following table shows the composition of the gases in the

	Gas entering the—								
	Glover tower.	1st ch.	2nd ch.	3rd ch.	4th ch.	5th ch.	6th ch.	Gay-Lussac.	Exit-gas.
SO_2	6·3	6·3	4·5	2·6	1·4	0·7	0·3	0·03	0·03
O required to form SO_3	3·2	3·2	2·2	1·3	0·7	0·35	0·11	...	...
N equivalent to Fe_2O_3 and SO_3 . . .	45·6	45·2	46·6	48·0	48·9	49·4	49·7	49·9	50·0
O in excess air . .	9·4	9·4	9·7	10·0	10·2	10·3	10·3	10·4	10·4
N in excess air . .	35·9	35·8	36·9	38·0	38·7	39·1	39·4	39·5	39·6
N_2O_4	...	0·12	0·12	0·13	0·13	0·13	0·13	0·13	0·01

different parts of a set of chambers, connected with a Glover and Gay-Lussac tower, calculated from a long series of observations. In the original the figures are given to three decimals per cent., but we reduce them to one decimal, the estimations certainly not being accurate even to that place. The nitre in the original is all calculated as N_2O_4, which is certainly wrong, and looking at the imperfection of former analytical methods, we must accept the figures for nitre with all reserve.

The next table shows the comparative condensation of acid in the six consecutive chambers:—

No. of chamber.	Acid made.	H_2SO_4 in acid made.	Excess water.	Per cent. of H_2SO_4 made in each chamber.
	Tons.	Tons.	Tons.	
1.	23·52	19·89	3·63	32·20
2.	22·59	18·68	3·91	30·26
3.	20·35	14·89	5·46	24·11
4.	10·23	4·35	5·88	7·04
5.	5·84	3·09	2·75	5·00
6.	2·19	0·86	1·33	1·39

The following table is taken from Mactear's paper, and shows the comparative condensation of the single chambers of various sets of sulphuric acid chambers:—

Chamber 1	31·50	32·20	32·5	38·4	34·1	33·8	52·4
„ 2	29·27	30·26	24·8	35·2	20·0	42·2	26·4
„ 3	18·71	24·11	19·5	15·6	19·7	22·6	16·5
„ 4	10·32	7·04	15·3	6·2	18·1	...	...
„ 5	6·45	5·00	5·8	3·2	7·3	...	...
„ 6	3·75	1·39	2·1	1·4	0·5	...	...
„ 7	.	...	...	...	0·3	...	
Tunnels	...	...	..	..	...	1·4	4·7
	100·00	100·00	100·0	100·0	100·0	100·0	100·0

Chamber 1	63·9	38·7	78·6	53·9	81·8	26·1	32·0
„ 2	36·1	33·6	21·4	36·9	17·8	31·3	29·0
„ 3	...	12·9	.	9·2	.	20·4	17·5
„ 4	...	9·8	...	...	..	11·8	13·7
„ 5		3·4	..		...	7·9	5·4
„ 6	...	1·6	..	.	...	2·4	2·2
„ 7	...	...		...		...	...
Tunnels	...	...	..	...	0·4	...	...
	100·0	100·0	100·0	100·0	100·0	100·0	100·0

Crowder (*J. Soc. Chem. Ind.*, 1890, p. 302) quotes the results obtained with gases taken from testing-holes in the connecting-pipes:—

	Lump-ore kilns.		Dust-kilns.	
	SO_2.	O.	SO_2.	O.
From Glover tower to No. 1 chamber	6·9	8·0	5·2	11·8
„ No. 1 to No. 2	4·4	7·5	2·4	11·8
„ No. 2 to No. 3	1·9	5·7	1·2	10·6
„ No. 3 to No. 4	0·4	6·1	0·6	10·2
„ No. 4 to Gay-Lussac	0·3	5·7	0·4	9·3

Another series from a Scotch works, with a set of six chambers:—

	SO_2.	O.
Glover tower to No. 1	6·32	12·55
No. 1 to No. 2	4·44	11·89
No. 2 to No. 3	2·63	11·28
No. 3 to No. 4	1·40	10·86
No. 4 to No. 5	0·70	10·61
No. 5 to No. 6	0·26	10·46
No. 6 to Gay-Lussac	0·035	10·38

Probably the most extensive and complete investigation on the phenomena taking place in the vitriol-chambers has been made by myself in conjunction with Dr Naef at the Uetikon Alkali-Works near Zurich, where a set of chambers was placed at our disposal for this purpose during a period of several months. From our Report thereon (*Chem. Ind.*, 1884, pp. 5 *et seq.*). I have already quoted in several places, *e.g.*, the methods employed for testing the gases (p. 580) and the observations of chamber-temperatures (p. 940). I here give a very short abstract of the important results obtained, which in all essential particulars have been entirely confirmed by a similarly extensive investigation made by Retter at a Hamburg works (*Z. angew. Chem.*, 1891, pp. 4 *et seq.*). The set of three chambers observed has been briefly described on p. 941. They were provided in twelve different places with complete sets of absorbing-tubes, large aspirators, and everything else required for making the most detailed and accurate analyses of the chamber-gases hitherto attained.[1]

The first six experiments proved that in a *normally* working set of chambers, containing a plentiful supply, but no excess, of nitre, the nitrogen oxides in the last two chambers did not contain any "free" nitrogen peroxide,[2] but their composition corresponded to that of nitrogen trioxide (nitrous anhydride). It had been assumed by Berzelius, and later on by R. Weber and by Hasenclever, that N_2O_3 was the real oxygen carrier, whilst most other chemists assumed that it was nitrogen peroxide; but Berzelius altogether confused N_2O_3 and N_2O_4, and Weber and Hasenclever, although they, of course, clearly distinguished between these two compounds, did not give any proof whatever of their assumption that the nitrous gas within the chambers is N_2O_3, not N_2O_4. The observations and analyses of Naef and myself for the first time gave a bases of fact to the statement that nitrous acid is the real oxygen carrier in the vitriol process. These observations have clearly established the fact that *in a normally working chamber no "free" nitrogen peroxide is found*, and Retter's observations (*cf.* p. 960) have entirely confirmed this. It is true that it was impossible to distinguish entirely between the single nitrogen oxides in the *first* chamber, as unfortunately no analytical methods are known by which this could be done in the presence of the large quantity of SO_2 existing in that place; all that can be done is to *calculate* the nitrogen oxides either into NO and N_2O_3, or NO and NO_2. But that the former, not the latter, is advisable, is proved by our further experiments, which showed that even when abnormally N_2O_4 was produced in the third chamber, yet the second chamber never contained any "free nitrogen peroxide."[1] *A priori* it is also most unlikely that in the first chamber, where the reducing action of SO_2 is so much more potent than in the second and third chambers, the nitrogen should be in a higher state of oxidation than in the latter chambers. It is therefore to be considered a fact *that the nitrogen oxides present in the last chambers correspond essentially to the composition of nitrogen trioxide, accompanied in the first chamber by nitric oxide*, NO.

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[1] It is true that even these analyses do not represent the absolute facts of the case. Some changes may, and even must, have taken place in the gases on their passage through the absorbing-apparatus; more especially the estimation of NO is not one of the most accurate operations. Nor can it be assumed that the samples of gas aspirated always represented the true average of that part of the chamber; and it was altogether impossible to be sure of following up one and the same batch of gas during its progress through the chambers. Our analyses cannot, therefore pretend to be authoritative in all details, but they may certainly be taken as representing the general working of the process. Sorel's criticisms of our methods are not very appropriate, as he does not suggest any better ones; his own plan of analysing nothing but the drip-acids is altogether misleading, as it takes no notice whatever of the proportions of oxygen and nitric oxide in the surrounding gases; and as it seems, from his description of the process, that he measured the reducing power of the acid by running a solution of potassium permanganate into the vitriol, instead of *vice versâ*, he must have found nitric acid even where none was present, as proved by me in 1877 (*Ber.*, vol. x. p. 1074).

[2] To avoid repetitions, we do not distinguish between NO_2 and N_2O_4, but call the mixture "nitrogen peroxide." "Hyponitric acid" is an antiquated expression. In the following abstract of the observations made in 1883, I

Another set of five experiments was made in this manner,

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retain the expressions "nitrogen trioxide" or "nitrous anhydride," then considered to correctly denote the facts of the case; but we now know that the N_2O_3 found by analysis is almost entirely dissociated into NO and NO_2 in the gaseous state.

[1] The expression "free nitrogen peroxide," in this and every subsequent case, means that portion of NO_2 which is in excess over that which is necessary to form N_2O_3 with NO, according to the equation: $NO + NO_2 = N_2O_3$.

that the quantity of nitre was increased far beyond the normal measure, so that a large volume of yellow vapours escaped from the Gay-Lussac tower. Under these anomalous circumstances, free nitrogen peroxide was found in the third, but never in the second chamber. *The chambers therefore contain free nitrogen peroxide only when the supply of nitre is abnormally high.* The formation of nitrogen peroxide must be regarded as a secondary reaction brought about in the following way:—With an abnormally high supply of nitre the oxidation of SO_2 into H_2SO_4 is almost entirely finished in the first chambers, as far as it can be driven (which is never up to the entire extinction of SO_2). There is hence very little sulphuric acid floating about as mist in the last chamber, and there is thus no impediment to the oxidation of NO going on to NO_2, which, as we shall see, does not take place in the presence of sulphuric acid. Moreover, the SO_2 still present in the cases here treated is of such minimal quantity (0·0004 to 0·002 per cent.), that its reducing action can scarcely be expected to be felt. The conclusion to be drawn from all this is that *free nitrogen peroxide, being absent in normally working chambers, cannot take any essential part in the formation of sulphuric acid in the vitriol-chambers.*

(When speaking of "normally" and "abnormally" working chambers, I always mean those terms to be understood as valid for the old style of working, with a chamber-space of at least 16 cub. ft. per lb. of sulphur. In the "forced or high-pressure style" (*production intense*), frequently referred to, where so much acid is produced in the chambers that only 12 cub. ft. of chamber-space or even less are allowed per pound of sulphur, an excessively large supply of nitre must be given, which at all other works would be called "abnormally high," but certainly not so under those exceptional circumstances. This leads to the regular appearance of nitrogen peroxide in the last chamber, and perhaps even of nitric acid in the nitrous vitriol of the Gay-Lussac tower. Sorel's statements in this respect are made uncertain by the fault in the analytical method employed by him (*cf.* above, p. 960, footnote), which would tend to make the proportion of nitric acid larger than it was in reality.)

Special experiments made by Lunge and Naef proved the following important facts:—1. Even with an abnormally low percentage of oxygen in the exit-gases (4 per cent.) the formation of free NO_2 takes place when an excess of nitre is sent into the chambers. 2. Even with an abnormally high percentage of oxygen in the exit-gas (8·18 to 9·19 per cent.) no free NO_2 is formed when the supply of nitre has been a normal one. This shows that *the quantity of air sent into the chambers has no influence whatever upon the formation of free nitrogen peroxide*, which, on the contrary, is *exclusively* caused by an excess of nitre.

In Lunge and Naef's paper now follow experiments on the losses of nitrogen compounds, which will be mentioned later on, and then experiments on the *distribution of the gases and the progress of the process in the chambers*. For this purpose eight sets of absorbing-tubes were fixed in various parts of the chambers, three of which were always worked simultaneously; in each place at least 20 l. of gases were aspirated for every test, the whole being finished within five or six hours. Five different complete sets of such observations were made, comprising both normal working and shortness of nitre in the chamber.

It would be too lengthy to give all the details of the analyses; they prove the following facts:—When the chambers are working in a *normal* way, the percentage of SO_2 in th gases decreases very quickly, and in the middle of the firs chamber has already fallen from 7 to 1·7 – 1·9 per cent., so tha about 70 per cent. of SO_2 must have been converted int sulphuric acid. From here to the end of the first chambe there is very little action, and only 4 per cent. of the origina SO_2 is here absorbed. When entering into the second chambe the reaction is suddenly revived, and in its centre the gase contain only 0·2 to 0·4 per cent. of SO_2, 20 per cent. of th initial SO_2 being absorbed here.

From this point to the end of the set the oxidation proceed very slowly, and never to the point of absolutely extinguishin the SO_2. The diagrams, Figs. 338 and 339, show this both fo the normal working order (in the thick line) and for workin short of nitre (the thin line)—the horizontal lines correspondin to the length of the chambers, the perpendicular lines to th percent. oxidation of SO_2 into H_2SO_4. There is also a dotte curve added, representing the progress of the process according to Hurter's theory (*cf.* below), which is seen to agree much better with the normal than the anomalous style of working.

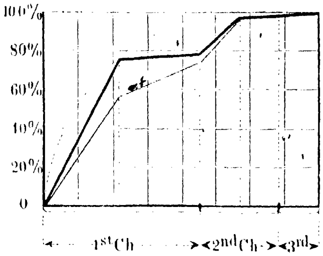

FIG. 338.

This agreement comes out still better in Fig. 339, representing the results obtained in another, intermediate, testing-place.

These experiments for the first time established a fact,

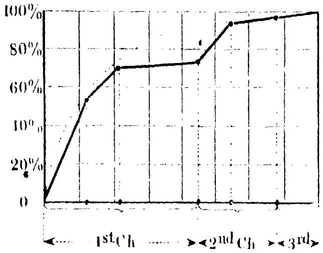

FIG. 339.

subsequently confirmed by all similar observations, the whole importance of which will appear below, viz., that the *conversion of* SO_2 *into* H_2SO_4 *takes place very quickly as far as the middle of the first chamber, then slackens very much, but is suddenly revived when the gases pass from this into the next chamber.* This fact was at the time explained merely by a better mixture of the gases, but we shall see that this explanation should be supplemented by other, and perhaps even more important considerations; and it has formed the first basis for the practical improvements proposed by myself, as described above (pp. 657 *et seq.*).

The observation made by Lunge and Naef at the Uetikon Works, that the reactions after slackening in the last part of the first chamber experience a sudden revival when the gases pass into the next chamber, has been confirmed by later observations of Naef's at the British Alkali-Works at Widnes (*Chem. Ind.*, 1885, p. 285), by Schertel at the Freiberg Works (*ibid.*, 1889, p. 80, and *Sächs. Jahresber. f. Berg- und Hüttenwesen*, 1890, p. 138), by Sorel (*Z. angew. Chem.*, 1889, p. 270), and Retter (*Z. angew. Chem.*, 1891, p. 4), and this must be looked upon as an established fact, the consequences of which for the theory of the vitriol-chamber process will be mentioned later on.

Another set of Lunge and Naef's experiments referred to the question *how far the gases get mixed up in their progress through the chamber.*

For this purpose the gas was aspirated and tested simultaneously from three places, lying in the same vertical line in the side of the first chamber, with the results given in the following table (*a* = top; *b* = middle; *c* = bottom).

	1.			2.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*
O . . .	9·63	10·37	8·45	5·15	5·62	5·18
N . . .	89·90	88·89	90·64	92·05	92·26	92·47
SO_2 . .	04·7	0·73	0·91	2·28	1·99	2·18
NO . .	...	...		0·05	0·06	0·06
N_2O_3 . .	...	...		0·10	0·09	0·11

	3.			4.			5.		
	a.	*b.*	*c.*	*a.*	*b.*	*c.*	*a.*	*b.*	*c.*
O . . .	6·68	6·07	6·04	5·98		5·42	6·37	6·27	6·27
N . . .	91·28	91·84	91·9[illegible]	92·64		93·17	91·77	91·70	91·76
SO_2 . .	1·86	1·94	1·88	1·20	.	1·20	1·86	[illegible]·03	1·97
NO . .	0·07	0·06	0·06	0·06	.	0·06	...	...	...
N_2O_3 . .	0·12	0·09	0·12	0·12	.	0·14	...	.	.

The differences in composition found between *a*, *b*, and *c* here are certainly but slight.

For the following experiments three lead tubes were passed hrough the chamber-top in the centre line, on the same cross section as the place on the sides on which the points *a*, *b*, *c* were situated, the three inner tubes reaching down to the same vertical height as the points *a*, *b*, *c*. Gas tests were taken at all six points at the same time, with the following results:—

	a.		*b*.		*c*.	
	Top.		Middle.		Bottom.	
	Inside.	Outside.	Inside.	Outside.	Inside.	Outside.
Exp. A—O . . .	7·34	7·12	7·76	7·36	6·93	7·39
N . . .	90·43	91·07	89·98	90·78	90·71	90·85
SO_2 . . .	2·03	1·66	2·08	1·67	2·18	1·58
NO . . .	0·08	0·08	0·08	0·10	0·10	0·10
N_2O_3 . . .	0·12	0·08	0·11	0·09	0·07	0·08
Exp. B SO_2 . . .	2·20	1·96	2·03	1·82	2·04	1·93

The difference in the composition of the gases here also is much slighter than was formerly assumed. More especially it was found that, contrary to former theories, the SO_2 is almost uniformly distributed at top, middle, and bottom. But it must be mentioned that there was, without any exception, considerably less SO_2 found at the outside places, near the chamber-walls, than in the centre of the chamber. This was noticed by Lunge and Naef at the time (*loc. cit.* p 17); they distinctly state that it proves that the reaction between SO_2 and O is rather stronger near the walls than in the centre of the chamber. A full explanation of this fact was only given several years later.

A last set of tests, in three places one above another in the first quarter of the first chamber, showed:—

	Exp. A.			Exp. B.		
	Top.	Middle.	Bottom.	Top.	Middle.	Bottom.
O . . .	6·59	6·26	6·79	5·89	6·07	5·81
N . . .	90·34	90·13	90·14	90·70	90·31	90·86
SO_2 . . .	3·07	3·61	3·07	3·71	3·62	3·33

The entering gases had contained 6·6 per cent. SO_2, so that at this place already about 50 per cent. of the SO_2 had vanished only 30 ft. from the front end of the chamber.

All these experiments (with which the observations of temperatures, pp. 940 *et seq.*, agree) *prove that the gases within the chamber are very quickly mixed up, whatever may be the cause of this, but that the mixture is not an absolutely equal one; there is always more* SO_2 *in the central part of the chamber than on the outside, or at top and bottom.* Retter (*cf.* p. 960) confirms this.

It must be especially insisted on that the differences between the analyses of various samples of gases are far greater than can be accounted for by analytical errors or by the inaccuracy of the methods; it was distinctly proved that in some parts of the same transverse section there is more SO_2, in some more O, in some more nitre, and it must be inferred without a shadow of doubt that there is in some places more moisture than in other parts of that section. Anybody who has experienced the difficulty of completely mixing two currents of gases, even when experimenting on a very small scale, will regard this as a matter of course. Those, therefore, who contend that Lunge and Naef's analyses prove an absolutely uniform composition of the gases in the same section of the chamber, and who from this infer the uselessness of a more intimate mixture, are altogether wrong, the above contention being erroneous; Schertel himself (*Sachs. Jahresber.*, 1890, p. 144), who had formerly adhered to the just-mentioned opinion, afterwards found that the mixture of the gases is not at all absolutely perfect.'

Thus Lunge and Naef's observations have refuted all the various theories according to which the sulphuric-acid making process either takes place principally close to the bottom-acid (H. A. Smith) or immediately below the top of the chamber (Mactear). They are, however, altogether compatible with Sorel's view (*cf.* below), which demands a stronger formation of acid near the chamber-walls, and with the following views of Abraham (*Dingl. polyt. J.*, 1882, vol. ccxlv. p. 416), concerning *the path taken by the gases within the chambers.*

After refuting the opinion pronounced by Schwarzenberg, according to which the burner-gases at once rise to the top of the chamber, and then gradually sink down in nearly horizontal layers, Abraham states his own ideas as follows:—The burner-gas, on entering the first chamber, meets a gaseous mixture whose temperature and composition differ but little from its own; it therefore spreads all over the front part of the chamber from top to bottom, and is slowly propelled by the draught along the chamber all over its transverse section. The formation of sulphuric acid also takes place regularly and equally at all points of each transverse section, taken at right angles to the length of the chamber, first rapidly, then more slowly. (This part of Abraham's theory cannot be accepted.) The heat produced by the reaction raises the temperature of the interior, whilst at the side walls and the tops this heat is carried off by radiation outside. Thus is produced a difference in the temperature and the density of the gases which must lead to their rising in the centre of the longitudinal section, and to their descending along the sides of the chamber. Since the cause of this difference of temperature is constantly acting, the just described movement goes on through the length of the chamber, and is modified only at the ends, both through their own cooling action, and through the contraction of the current produced by the connecting-pipes. Hence *the gases travel in vertical layers at right angles to the length of the chamber, from the front to the back end, but each single gaseous molecule describes a spiral line, whose axis is parallel to the length of the chamber.*

This is of course only a general expression of the path of the gases within the chambers, and is modified locally by special circumstances; but it accounts for the approximate equality of the composition of the gases and temperatures observed in Lunge and Naef's, and even in Mactear's experiments.

Improvements proposed for Acid-chambers in accordance with the above-described Investigations.

Hartmann and Benker (*Z. angew. Chem.*, 1903, pp. 861 to 869) accept this theory and base thereon their arrangements for producing the proper movement of the gases by means of a fan, placed at the end of the system, by which means they realised a very strong "intense production." Th. Meyer (*ibid.*, p. 927) strongly contradicted their assertions.

Porter (*J. Soc. Chem. Ind.*, 1903, p. 476) made some experiments with a glass model chamber from which he concluded that the gases should be admitted into the chamber at the bottom, and the steam at either end, so as to intermix with the centre core of both incoming and outgoing gases.

Rabe (*Z. angew. Chem.*, 1910, pp. 8 to 12, Ger. P. 237561), starting on the assumption of the correctness of Abraham's theory, proposed to introduce the gases into the chamber in the direction of those spiral lines, that is in middle of the front wall, with an upward direction, so that the gases should at once rise to the top, then descend to the bottom and thus start on the double spiral lines; special ways can be made for them by branching off towards the sides. The movement of the gases in the desired direction is promoted by sprays of water or steam, not opposite the direction of the gaseous current, as Hartmann and Benker prescribe (*ibid.*, 1903, p. 865), but parallel to that direction, for which purpose they are placed so as to play against the side walls, or in the centre upwards, so that the water only arrives at the bottom when it has been converted into sulphuric acid. As this will not take place very equally all over, the sprays are better made with dilute acid. This way of increasing the spiral movement by means of properly arranged sprays may also be followed with Meyer's tangential chambers (p. 622), both for the upper and especially for the lower part of the chamber.

Th. Meyer (*Z. angew. Chem.*, 1910, p. 555), referring to his above-mentioned former paper on this subject, says that Rabe's views cannot be accepted until tried on a practical scale, both concerning the way of introducing the gases into the chamber, and still more so concerning the placing of water- or sulphuric acid sprays in the direction prescribed by Abraham's theory. He states that already in 1900, when the first "tangential chambers" were built, the steam-jets were placed tangentially so that there would be no novelty in doing the same with jets of liquid; but his own experiments in that line did not show anything like the expected increase in the spiral movement, and the expense of raising and injecting all the chamber-acid in this way is quite prohibitive. For tangential chambers there is no need of such an artificial means of increasing the movements of the gases. Rabe (*ibid.*, p. 1135) replies to him that Porter's experiments with a glass model (*suprà*, p. 968) are inconclusive, as they were made with cold gases and under circumstances otherwise entirely different from those of the vitriol chambers. Rabe upholds his views and again advocates the introduction of a large quantity of chamber-acid in the form of a spray, in order to produce an appropriate movement and mixture and cooling of the gases, more particularly for tangential chambers.

On the other hand, Beskow (*Z. angew. Chem.*, 1911, pp. 200 to 206) experimentally investigated the movement of the gases in ordinary vitriol-chambers, in the same way as he had previously done with Meyer's tangential chambers (*suprà*, p. 625). He did not in this case find currents corresponding to Abraham's theory, but he conceived the idea of producing such currents by dividing the gases, before entering the chamber, into ten smaller tubes and blowing them into the chamber near the bottom in various places. He also took out a Swedish patent for this (No. 28332), but a chamber built on this plan at Helsingborg did not realise his expectations as to increased production and decreased consumption of nitre. Later on Rabe's system was published, without taking notice of Beskow's previous work in this direction.

Olga Niedenführ (Ger. P. 189283) introduces the gases into the chambers on the top by central or symmetrically arranged openings, and after they have spread equally all over the chamber, without any mechanical device, they leave the chamber by central openings in the bottom. By her Ger. P. 189330 she applies the same way of introducing and taking out the gases also to reaction-towers, and her Ger. P. 189834 shows how a spiral movement of the gases may be brought about in chambers of circular section by means of spirally arranged partitions (*vide suprà* her circular chamber).

Carbon Dioxide in Chamber-gases.

It is generally assumed by manufacturers that carbon dioxide exercises a very injurious action in the lead chambers, and it is principally on this account that "coal-brasses" are not considered a good raw material for the production of sulphuric acid (pp. 65, 458). If this is really the case, it is all the easier to understand why the proposals for filling the lead chambers with coke have been unsuccessful. The reason why it should be so is not yet clear. Some practical men assume that the CO_2 forms distinct layers, preventing the intimate contact of the gases with each other and with the bottom-acid; but I am not aware of any direct observations on this point, except in one case where blende containing very much carbonates was worked, when it was found by many gas-analyses that the carbon dioxide accumulated in the corners and other "dead" places, whilst the main stream of the gases contained much less CO_2. This subject ought to be further investigated, especially as I know of a Bohemian works where sulphuric acid is made from material containing 10 per cent. of bituminous substances, without any special trouble being experienced.

Duration of Passage of the Gases through the Chambers.

Calculations have been made as to *how long the gases remain in the lead chambers* before the manufacture of sulphuric acid is complete. This subject is treated at length in our first edition, vol. i. pp. 455 *et seq.*; here we will only mention that Schwarzenberg calculates that the gases pass through the chambers in five and three-quarter hours, Bode that they take three and three-quarter hours, and I myself (assuming a chamber-space of 20 cub. ft. per lb. of sulphur and burner-gases with 8 per cent. SO_2) reckon two and three-quarter hours. It is also there calculated that, assuming a consumption of 4 parts of pure sodium nitrate to 100 parts of sulphur burnt, the nitre-gas does its oxygen-carrying work 130 times over before it is lost in some shape or another. Sorel calculates that in a system working on the "high-pressure" plan, with only 0·7 cb.m. per kilogram, or 11·2 cub. ft. per lb. of sulphur burnt (in winter), the gases take only one hour thirty-four minutes to pass through the chambers.

Testing the Chamber-exits.

Apart from the ultimate check on the process afforded by frequent estimations of the yield of acid and the consumption of nitre, of which we shall speak later on, it is very desirable, and has even been for some time past required by law, to control the quantity of acids escaping from the vitriol-chambers into the atmosphere. So far as "low-level escapes" are concerned, that is the gas blowing out of pyrites-kilns, potting-holes, accidental leaks in the chambers, and so forth, it is not possible to estimate them directly; but it is just these kinds of escapes that are most readily perceived, and although they may be very troublesome to those residing in the immediate neighbourhood, they hardly ever amount to any considerable percentage of the sulphur burned.

It is very different with the gases escaping from the end of the whole system into the atmosphere, whether it be through a simple pipe or a Gay-Lussac tower, or the chimney. These "high-level escapes" may cause a serious manufacturing loss, and they may also amount to a real nuisance to the parties living near the works, although in most instances only temporarily, especially in unfavourable weather. Before the introduction of nitre-recovery apparatus the loss, both of the acids of sulphur and those of nitrogen, must have been far more considerable than now, as the whole style of working inevitably tended in that direction; but nothing certain can be stated with regard to this, as no observations on the acidity of chamber-exits were formerly made, and at present all well-arranged works do recover their nitre. In this case the losses will not be quite so serious, but they do exist all the same, and that to a greater extent than was formerly supposed.

Among the first who drew attention to the necessity of regularly testing the chamber-exits for their acidity were Mactear (*Chem. News*, vol. xxxvi. p. 49) and G. E. Davis (*ibid.*, vol. xli. p. 188).

Control of the acids escaping from the chambers into the atmosphere has been made compulsory in England, since, in 1881, it was enacted by law that the total quantity of sulphur acids escaping from an alkali-works should not exceed 4 g. per cubic foot, expressed in terms of sulphuric anhydride, SO_3 (sec. 8 of the Act). About nitrogen acids or nitric oxide nothing is enacted, probably because the quantity escaping from alkali-works is never so great as to cause a nuisance, but it is all the more important for the manufacturer himself to know how much nitre he is losing in this shape; moreover, in testing the chamber-exits it is but little additional trouble to include the nitrogen acids.

In Germany, by an order in Council of 1st July 1898, the maximum amount of total acids in the exit-gases of works burning pyrites has been fixed at 5 g. from blende 8 g. per cubic metre, calculated as SO_3.

The British Government Inspector's Reports show that the real escape of acid gases from the exits of sulphuric-acid works is far below the maximum prescribed by the Act. The average amount of acids escaping, calculated in grains of SO_3 per cubic foot, were in 1887, 1·500; in 1888, 1·490; in 1889, 1·370; in 1900, 1·198; in 1901, 1·186; in 1909, 1·162 (in the same year the exit-gases from the concentration and distillation of sulphuric acid averaged 0·773 grains per cubic foot).

It seems to be lawful, where the gases cannot be sufficiently diluted down to the standard escape by means of fuel gases from other parts of the process, to do this by atmospheric air admitted to the chimney (*Alkali Inspector's Report*, No. 38, p. 76).

Two systems may be employed for controlling the acid escapes—that of taking several separate tests through the day, and that of continuously aspirating some of the gas through a set of absorbing-apparatus, and measuring the quantity of gas passed through them.

The unreliability of the first system is too patent to be enlarged upon; it is hardly applicable at all to night-work, to begin with. Hence the *continuous-testing system* has been generally adopted, and this at many works in the very complete shape given to it by Mr Mactear (*loc. cit.*). His apparatus consists of a water-jet pump (of the system invented by Dr Sprengel, but commonly called "Bunsen pump") for aspirating the gases, a set of absorbing-tubes, and a gas-meter to measure the volume of the residual gases after absorption. The whole, including the cocks and connections, is enclosed in a locked closet to prevent their being tampered with. The meter is fixed with an index so arranged that by observing the reading for one minute the rate of passage per hour is given by direct indication, so that the rate of aspiration is easily arranged. Mactear at that time proposed caustic soda and ammonia as absorbents, to be titrated for SO_2 with permanganate; but this would yield quite wrong results, far below the truth, as sodium sulphite is rapidly oxidised by the oxygen passing through the solution.

Mactear's apparatus is very efficient, but it is very costly.

and any such delicate apparatus as a gas-meter is very liable to get out of order in such proximity to acid vapours. Hence at most places cheaper and simpler forms of aspirators have been adopted. One of the simplest is represented in Fig. 340. It consists of two glass bottles, I. and II., each provided with a

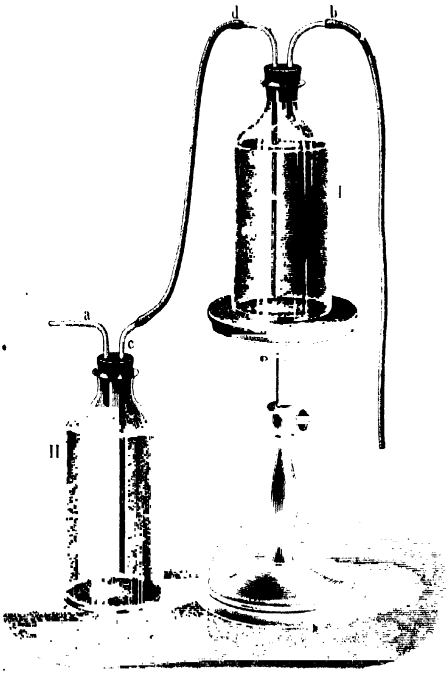

FIG. 340.

twice-perforated india-rubber cork, through which passes one elbow-tube (*a*, *b*) ending just below it, and another (*c*, *d*) reaching down to the bottom of the bottle. The tubes *c* and *d* are connected with an elastic tube; another such tube connects either *a* or *b* with the absorbing-apparatus. One of the bottles, say I., is placed so that its bottom is raised above the top of II.

If now *b* is connected with the absorbing-apparatus, and the air is sucked from *a* for a moment, the siphon formed by *c*, *d* and the elastic tube begins to run, gas being aspirated from *b*. When the contents of I. are run out, the elastic tube is detached from *b*, the position of the bottles is reversed so that II. now stands higher, and the elastic tube is put upon *a*; the connection between *c* and *d* is not touched. Usually the siphon begins to act again of its own accord; otherwise it is started by sucking for a moment at *a*. The quantity of water running out of the bottles at each turn is determined once for all.

The plan just described has the drawback of requiring an attendant to change the position of the bottles, and is hence hardly convenient enough for continuous testing. For this purpose, if a meter is to be dispensed with, a vessel of large capacity, say several cubic feet, should be provided, sufficient to serve for twenty-four hours without special attendance. Such a vessel can be made of glass, stoneware, or wood lined with lead; it should be cylindrical and provided with a gauge for measuring the height of the water within; in order to act quite equally it should be on the principle of a Mariotte's bottle, as described on p. 709. The form adopted by Younger (*J. Soc. Chem. Ind.*, 1887, p. 347) has no special advantages.

An excellent apparatus has been described by W. G. Strype (*Trans. Newc. Chem. Soc.*, 1880, vol. iv. p. 357). We will here give a description of it, abridged from the inventor's own words, with two drawings, Figs. 341 and 342, showing it in two different conditions; but it is unnecessary to say that some details, such as the absorbing-apparatus, may be varied without any detriment to the principle.

Fig. 341 shows it in the process of being charged with water and having the old solution removed; and in Fig. 342 it is shown as in ordinary work. The measuring-vessel E is of some 5 cub. ft. capacity. The supply of water to charge this vessel is through the cock A, communicating with the vessel by means of the large pipe B, C, which is carried up to the open end at D, and to such a height as to ensure that too much pressure is not thrown on the apparatus when it is being charged; if too much, of course the water will overflow at the open end, D. The air or residual gas remaining in the measuring-vessel after each period of absorption escapes, when it is being refilled, through the tube *a a′ a″* into the lower vessel F, under the pressure of a small head of water of about one foot, and as the escaping air communicates by means of the tube *f b b′* with the test-bulbs, the pinch-cock at *c* being opened, the small pressure thus expels

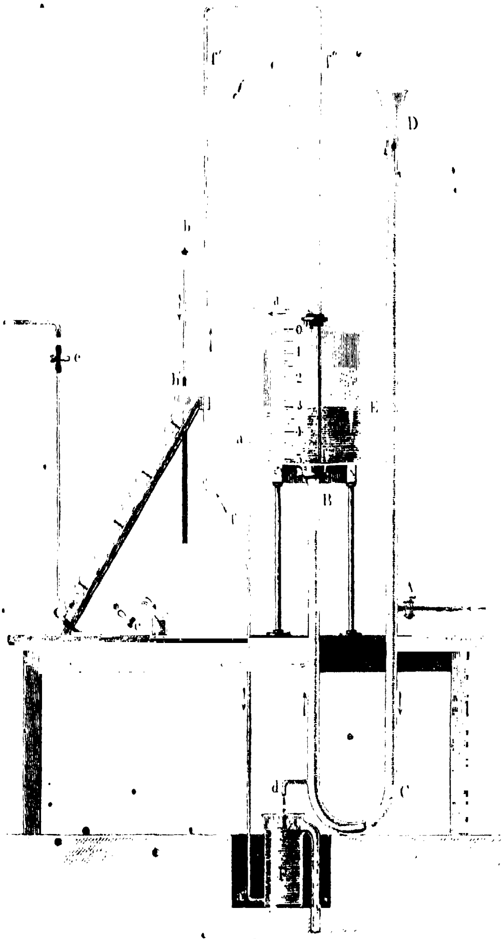

Fig. 341.

the old absorbing-solution as shown in Fig. 341. When the vessel E is full, the old absorbing-solution being driven out of

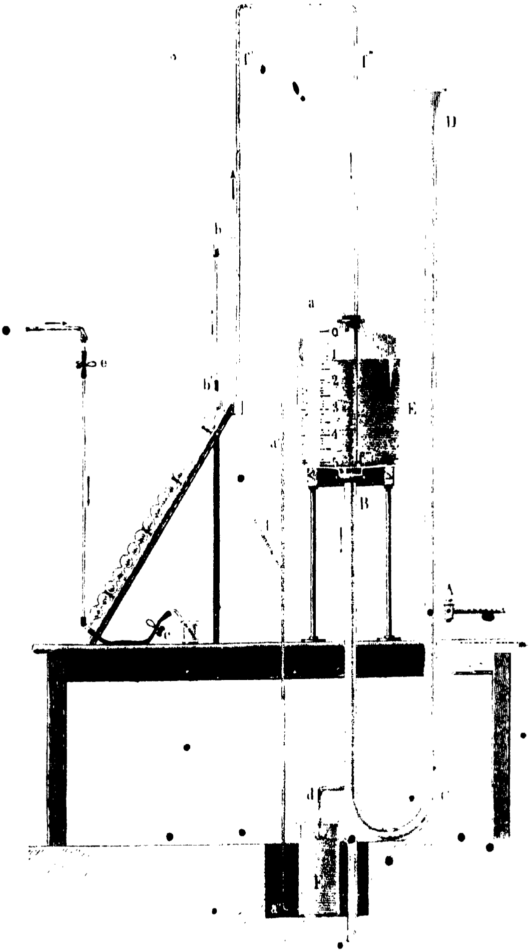

FIG. 342.

the bulbs, the cock A is shut, and the excessive water drains away from the small drip-pipe *d*, thus emptying all the connections to the condition shown in Fig. 341; and the pinch-cock at *c*, and also the regulating pinch-cock on the pipe at *e*, which communicates with the chamber-exit, being closed, the flow ceases, and equilibrium is established by the apparatus being under the small vacuum due to the head of water in the vessel E over the open drip-pipe *d*. The pinch-cock *c* is now opened, and the india-rubber tube hanging from it is dipped into a beaker containing the test solution, which is now drawn up into the bulbs by the vacuum. When the charge is complete the pinch-cock at *c* is closed, and the regulating pinch-cock *e* opened to the required extent so as to admit the escaping gases from the chamber-exit to enter the apparatus; and absorption of the acid follows, together with accurate measurement of the volume dealt with; the residual gas passes into the measuring-vessel through the tubes *b' b*, *f' f'' f'''*. The latter tube is carried down at *f'''* close to the bottom of the vessel E, in order to secure a uniform flow of gas with the varying head due to the gradually diminishing level of water in the vessel, in the manner too well known to need further reference, and it is to secure this point that a difficulty arises in arranging such an apparatus. The tube *a a' a''* must be sealed off when the apparatus is at work if the flow of escape through the absorbing-solution is to be at a uniform rate, and this is accomplished by a very simple plan. Upon turning on the water at A to charge the apparatus the water runs down *a a'*, and when as low as the inclined pipe at *f*, air glides upwards, and the small quantity of water in the inclined pipe *f* also drains away; without this contrivance there would be a small quantity of water driven over into the test-bulbs each time the apparatus was charged, but the tube being placed in a diagonal direction entirely prevents this.

The proportions and relative positions of the various parts are accurately shown to scale in the drawings, and it is important this should be carefully attended to in constructing the apparatus.

The arrangement to contain the absorbing-solution consists of a series of 30 bulbs, each about 1⅛ in. diameter, with small and short necks between them; the bulbs are made in sets of 10 each; 3 sets are coupled together with small pieces of india-rubber tubing, and the charge of 300 c.c. occupies about 22 of them, leaving a little free space in the upper part of each.

A large bulb of some 4 in. diameter is placed, as shown, at the head of the bulbs, to catch any of the absorbing-solution in case it should be drawn up through all the smaller bulbs by accidentally turning on the flow of gas with too much violence in starting the apparatus. The solution used in this way contains 100 c.c. normal caustic soda, diluted to 300 c.c. coloured with litmus (methyl-orange must not be used in this case as it is destroyed by nitrous acid). The drain-pipe *d* is always open and is of small aperture, but sufficient to more than carry away the water as it drains from the measuring-vessel in ordinary working, and thus a constant vacuum is maintained.

The apparatus is preferably constructed of glass, with india-rubber junctions; but of course it can just as well be made with an iron or lead measuring-vessel and lead pipes, a water-gauge being employed to observe the level of the water in E.

The staunchness of all the parts is ascertained, when the apparatus has just been charged, by shutting off the pinch-cocks *c* and *e*, and seeing that no water drains from the open pipe *d*. In charging, the water freely flows from *d*, but the aperture being small this does not appreciably interfere with the filling of the vessel E.

Whatever be the system of aspirating the gases, they must be passed through certain *solutions to absorb the acids* contained therein as completely as possible. The different acid compounds of sulphur are estimated together, as well as those of nitrogen, whatever degree of oxidation they may possess. The following *prescriptions* agree in the main with those worked out by Hurter and published *by the British Alkali Makers' Association* in 1878.[1] A continuous test over twenty-four hours is taken of the gases escaping from the exit-pipes of the Gay-Lussac towers, aspirating at least 1 cub. ft. per hour by means of any aspirator acting at a constant rate, and recording the volume of gas (= V) by means of gauging the aspirator or by a gas-meter. The volume V is reduced to 0 C. and 760 mm. pressure (= 32° F. and 29·92 in.) by the tables contained in

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[1] These prescriptions, with a few improvements in analytical details, are also given in Lunge's *Technical Chemists' Handbook*, 1910, pp. 118 *et seq.*

Lunge's *Handbook*, pp. 38 *et seq.*,[1] and is now called V'. In order to allow comparisons, the number of cubic feet of chamber-space per pound of sulphur burnt and passing into the chambers is recorded, excluding towers, but including tunnels, the amount of sulphur being taken by the weekly average, stating the distance of the testing-hole from the point at which the gases leave the Gay-Lussac towers. The absorption-apparatus consists of four bottles or tubes (Fig. 343[2]), containing each not less than 100 c.c. of absorbing-liquid, with a depth of at least 3 in. in each bottle, the aperture of inlet-tubes not to exceed $\frac{1}{50}$ in. in diameter and to be measured by a standard wire. The first three bottles contain each 100 c.c. of normal caustic-soda solution (31 g. per litre), the fourth 100 c.c. distilled water. The caustic soda must be free from nitrogen acids. The gases are tested (1) for total acidity, stated in grains of SO_3 per cubic foot of gas, or else in grammes per cubic metre; (2) sulphur acids; (3) nitrogen acids—both stated in grains of S and N per cubic foot (or grammes per cubic metre). The analysis is carried out as follows:—The contents of the four bottles are combined, taking care not to unnecessarily augment the bulk of the liquids, and are divided into three equal parts, one of which is reserved for accidents, etc. The first part is titrated with normal sulphuric acid (49 g. H_2SO_4 per litre) to ascertain total acidity. The number of cubic centimetres of acid

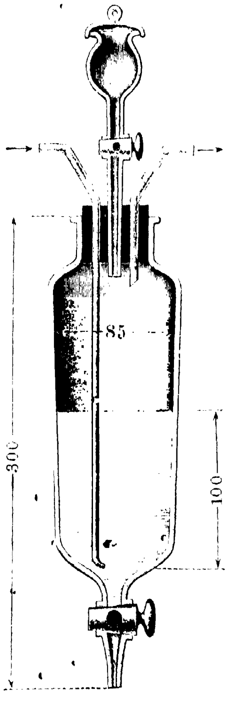

FIG. 343.

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[1] The law prescribes the cubic foot to be measured at 60° F. and 30 in., which necessitates the use of other tables or factors than those mentioned in the text, but the difference is hardly perceptible, and is within the limits of experimental error.

[2] Taken from Jurisch, *Schwefelsäurefabrikation*, p. 224.

necessary for neutralisation is called x. The second part of the liquid is gradually poured into a warm solution of potassium permanganate, strongly acidified with pure sulphuric acid. A small excess of permanganate must be present, and must be afterwards reduced by the addition of a few drops of sulphurous-acid solution, until only a faint red tint is visible. Now all nitrogen acids are present as HNO_3, but no excess of SO_2. The HNO_3 is estimated by its action on $FeSO_4$. Twenty-five c.c. of a solution, containing per litre 100 g. of crystallised ferrous sulphate and 100 g. pure sulphuric acid, are put into a flask, 20 to 25 c.c. pure concentrated sulphuric acid is added, the mixture is allowed to cool, and the other mixture, treated with permanganate, etc., is added. The flask is closed by a cork with glass tubes. A current of CO_2 passes through and issues beneath the surface of some water, to prevent entrance of air. First, all the air is expelled in this way by an apparatus evolving CO_2 by constant action; then the solutions are introduced, and the contents of the flask are heated to boiling, till the dark colour produced by the formation of NO has changed to a clear light yellow. This lasts a quarter of an hour to one hour, according to the quantity of HNO_3 present and that of the sulphuric acid added. The unoxidised ferrous sulphate is titrated by a semi-normal permanganate solution (yielding 0·004 g. oxygen per cubic centimetre); the cubic centimetres used $= y$. Since the titre of the iron solution changes pretty quickly, it should be tested daily by taking out 25 c.c. with the same pipette as serves for the above-described operation, and ascertaining the amount of permanganate required for oxidising it, $= z$ c.c. The magnitudes sought are found by the following equations:—

1. *Total Acidity* in grammes per cubic metre:

$$SO_3 = \frac{0{\cdot}120(100 - x)}{V'}.$$

2. *Sulphur* in grammes per cubic metre:

$$S = \frac{0{\cdot}008(600 - 6x - z + y)}{V'}.$$

1. *Total Acidity* in grains per cubic foot:

$$SO_3 = \frac{1{\cdot}852(100 - x)}{V'}.$$

2. *Sulphur* in grains per cubic foot:

$$S = \frac{0{\cdot}12346(600 - 6x - z + y)}{V'}.$$

3. *Nitrogen* in grammes per cubic metre:

$$N = \frac{6{\cdot}007(z - y)}{V'}.$$

3. *Nitrogen* in grains per cubic foot:

$$N = \frac{0{\cdot}10803(z - y)}{V'}.$$

If the nitrogen acids are not to be separately estimated (and the Alkali Act does not require this to be done), the above prescriptions can be extremely simplified. It is only necessary to employ the apparatus shown on p. 572, Fig. 156, and intended for testing the burner-gases for sulphur acids, or else one of the absorbing-apparatus to be mentioned below is employed. The apparatus is charged with 100 c.c. of normal caustic-soda solution, coloured with phenolphthalein, which acts equally upon SO_2 and H_2SO_4, and this is re-titrated with standard acid. The caustic-soda solution should be as free as possible from carbonate, as CO_2 acts upon phenolphthalein as well. The formula for calculation is then No. 1 divided by 3, that is:—

$$SO_3 = \frac{0{\cdot}040(100 - x)}{V'} \text{ g. per cubic metre,}$$

$$= \frac{0{\cdot}617(100 - x)}{V'} \text{ gr. per cubic foot.}$$

When the object of testing the exit-gases is merely to ascertain the total acidity, in view of the requirements of the law (p. 579), it is sufficient to pass a certain volume of the gas through a solution of hydrogen peroxide, which oxidises the SO_2 to H_2SO_4, and then to titrate the whole of the acids with caustic-soda solution and methyl-orange, and calculate them as SO_3. In a very exhaustive paper (*J. Soc. Chem. Ind*, 1902, p. 1490) R. F. Carpenter and Linder prove that the best way of proceeding is to employ for the absorption a mixture of 1 vol. semi-normal caustic-soda solution and 10 vols. hydrogen peroxide solution, which is afterwards re-titrated by phenolphthalein at a boiling heat, or by methyl-orange in the cold. In this case the nitrogen acids proper are also absorbed, but NO is only very little acted upon. They believe that thus certain sulphazotised bodies, present in chamber escape gases, are also dealt with. The nitrous smell, sometimes observed in the gases discharged from the bellows aspirator, they assume to be caused by the reaction:

$$H_2O_2 + 4HNO_2 = 2HNO_3 + 2NO + 2H_2O.$$

H. J. Watson (*J. Soc. Chem. Ind.*, 1903, p. 1279) generally confirms Carpenter's and Linder's results and conclusions, especially the necessity of employing both alkali and hydrogen peroxide. He suggests using five absorbing-vessels; the first two being charged with hydrogen peroxide and the other three with alkaline hydrogen peroxide. The first show the acidity of the gases, the last three the nitre lost through that formerly neglected compound existing in chamber-gases.

The *shape of the absorbing-vessels* is not at all indifferent. When employing ordinary bottles with simple glass tubes dipping below the liquid, the absorption is often incomplete, even if several bottles are used in succession, which causes considerable pressure. The use of very narrow inlet-tubes, as prescribed in the *Alkali Makers' Instructions* (see above, p. 980), lessens, but does not entirely avoid the evil, of incomplete absorption. The potash-bulbs used in organic analysis cannot be employed, because it is too difficult to empty their contents without any loss.

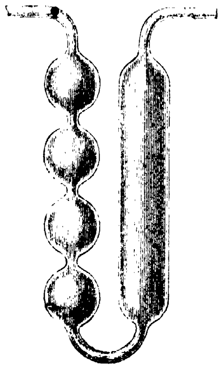

FIG. 344.

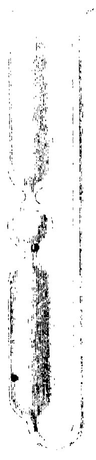

FIG. 345.

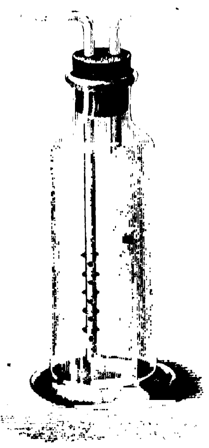

FIG. 346.

The absorption is better when using Mitscherlich's tubes (Fig. 344), of which Todd's tubes (Fig. 345) are but a slight modification. The shape of absorbing-bottle shown in Fig. 346

serves also very well. Better than these is the Pettenkofer tube as modified by myself (Fig. 347), and still better a 10- or 15-bulb-tube, as shown in Fig. 348, one of which generally suffices for complete absorption.

Ordinary absorbing-bottles fail of their purpose where white mists of acid in a vesicular form have to be dealt with, as in the case of the gases from overhead-fired pans or beaker-apparatus for rectified vitriol (*cf.* Chapter IX.). In these cases the bottles may be shaken a hundred times and upwards without entirely removing the white mist. The Alkali Inspectors have, however, elaborated a bottle performing this service most efficiently. It is shown in Fig. 349, where we notice the absorbing-bulb, containing inside a number of india-rubber rings (cut from ordinary small tubing). The gases pass through the central tube *a*, by small holes *d* near its closed end, into the bulb *b*, and before they issue through the holes *c c* they are broken up into small bubbles by the india-rubber dippings, which are washed by the movement of the liquid in the apparatus, and thus produce a thorough scrubbing of the gas.

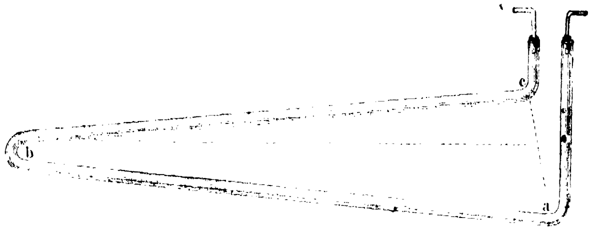

FIG. 347.

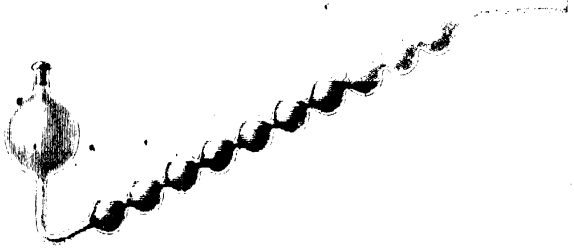

FIG. 348.

The upper bulb is ¾-in. wide, the lower ⅜-in., the bottom-opening ¼-in.; these proportions should be observed to attain the object. Exit-tube *e* is filled with glass-wool.

Nitric oxide can be (and generally is) present in the gases after passing through the absorbing-bottles, as its oxidation to NO_2, when it is strongly diluted, is an extremely slow process (*cf.* 40*th Alkali Report*, p. 27). It can be estimated in an absorbing-tube (Fig. 347), or better in a bulb-tube (Fig. 348), interposed between the tubes of the apparatus serving for estimating the acids and the aspirator. The bulb-tube is charged with 30 c.c. of seminormal permanganate solution and several cubic centimetres of sulphuric acid. The gas is passed through for twenty-four hours, and the tube emptied and washed out. Now add 50 c.c. of ferrous-sulphate solution, corresponding to 2*x* permanganate, and re-titrate the decolorised liquid with permanganate. (If a precipitate of manganese peroxide has been formed in the absorbing-tubes, rinse the tubes with some of the iron solution.) The quantity of the permanganate last used is called *u*. The NO has altogether consumed (30+*u*−2*x*) c.c. of permanganate, giving:—

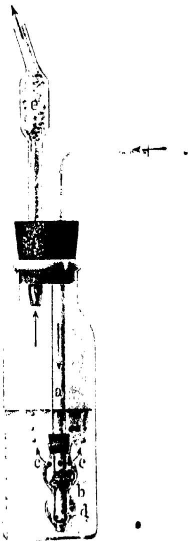

FIG. 349.

In grammes of nitrogen per cubic metre of the volume V′.

$$N = \frac{0{\cdot}007\,(30 + u - 2x)}{3V'}$$

In grains of nitrogen per cubic foot.

$$N = \frac{0{\cdot}10803\,(30 + u - 2x)}{3V'}$$

The quantity of nitric oxide present in chamber exit-gases may be at times rather considerable without attracting notice as it oxidises only very slowly when strongly diluted with inert gases. This makes some of the absorbents proposed, as hydrogen peroxide or a mixture of strong sulphuric with nitric acid, practically useless for the estimation of NO, as proved by myself by many laboratory experiments. The paper of Carpenter and Linder, quoted p. 982, corroborates this

Just for this reason I first proposed in 1881 the use of an acid solution of potassium permanganate and the apparatus described here. Even this process requires a very good absorbing-apparatus and a very slow stream in order to take all the NO out of the gases.

The apparatus and methods described by Lovett (*J. Soc. Chem. Ind.*, 1882, p. 210) may be consulted by those specially interested in this subject, but call for no special remark here. This holds good also of the papers of G. E. Davis (*Chem. News*, xli. p. 188) and Pringle (*J. Soc. Chem. Ind.*, 1883, p. 58).

The gas collecting in the aspirating-vessel of any of the above-described apparatus, being an average sample of the exit gases free from acids, is very conveniently employed, in preference to samples taken at random over the day, for *estimating the oxygen* contained in the exit-air. This estimation has been previously described (p. 578), and we have here only to show how the estimation of oxygen in the exit-gas may be used for *ascertaining the quantity of sulphur burnt*, expressed in grammes per litre of the exit-gas, so that the quantity of sulphur lost in that gas may be put in direct comparison with the total sulphur used. For this the following formula has been proposed by me in *Dingl. polyt. J.*, ccxxvi., p. 634:—

$$(20{\cdot}95 - a) \times 0{\cdot}009637 \times \frac{1}{1{\cdot}00367\ t} \times \frac{h}{760} = x.$$

Here a denotes the percentage of oxygen in the exit-gas, t its temperature, h the barometrical pressure in millimetres, x the total quantity of the sulphur actually burnt, expressed in grammes per litre of the exit-gas; with this the quantity actually found should be compared, in order to find the percentage of loss. It should not be overlooked that no account is here taken of the sulphur remaining in the cinders.

Coleman (*J. Soc. Chem. Ind.*, 1906, p. 1201) describes and illustrates his plan of *graphically recording* the work of vitriol-chambers, which indeed appears to be very useful, although rather complicated.

Knorre and Arndt (*Berl. Ber.*, 1899, p. 2136) mix the gas with hydrogen and pass it very slowly through a bright red heated platinum capillary which causes a contraction to the amount of $\frac{3}{2}$ of the volume of the nitric oxide originally present, according to the reaction :—

$$\underset{4\text{ vols.}}{2NO} + \underset{4\text{ vols.}}{2H_2} = \underset{0\text{ vols.}}{2H_2O} + \underset{2\text{ vols.}}{N_2}.$$

THEORY OF THE FORMATION OF SULPHURIC ACID BY THE VITRIOL-CHAMBER PROCESS.

When describing in previous chapters the behaviour of sulphur dioxide towards the various nitrogen compounds in the presence of water, sulphuric acid, etc., and the formation and decomposition of nitrososulphuric acid, we have been obliged repeatedly to forestall theoretical considerations; but these will now be brought forward connectedly and in detail.

We must from the commencement bear in mind the fact that during the burning of sulphur, whether in the form of brimstone, pyrites, or blende, etc., substantially sulphur dioxide (SO_2) alone is formed; the formation of sulphuric anhydride or acid, always occurring at the same time (at least in the case of pyrites), is not taken into account here, being merely a secondary reaction, and not exempting us from the task of explaining the oxidation of the sulphur dioxide in the lead chambers. That this does not take place to an appreciable extent by the direct action of the atmospheric oxygen, may at the outset be taken as established. But it is just as certain that the oxygen of the nitre introduced into the process does not suffice to account for it; for the sulphur dioxide from 100 parts of sulphur requires another 50 parts of oxygen in order to be oxidised to sulphuric acid, which would correspond to 81·5 parts of nitrate of soda even if this compound were reduced to nitrogen. But it is well known that, under favourable conditions, only $\frac{1}{30}$ to $\frac{1}{25}$ of the above quantity of nitre is used; and this fact must now be explained.

The first theory on this subject was propounded as early as 1806, by Clément and Désormes (*Ann. Chim.*, lix. p. 329); and it must be owned that they had observed most of the essential facts, and connected them by a theory which has not had to be entirely abolished, but only to be modified with the growth of our knowledge. They had studied the behaviour of sulphur dioxide towards a mixture of nitric acid and atmospheric air; and they proved that, even in the crude process then in use (where a mixture of brimstone, saltpetre, and moist clay was heated in a furnace and the gaseous products were conducted into the lead chamber), considerably more oxygen was transferred to the sulphur dioxide than the saltpetre contained. They already explained this fact in substantially the same way as it is explained nowadays, viz. thus:—From the nitre-gas oxidised by atmospheric oxygen, and from the sulphur dioxide, sulphuric acid is generated, whilst the nitre-gas is re-formed. The nitric acid is only the instrument for the complete oxidation of the sulphur, which in doing its work is not destroyed; for its "basis," the nitre-gas takes up oxygen from the atmospheric air in order to present it to the sulphur dioxide in a suitable state; but it remains in its original state at the end of the process of forming the sulphuric acid. The presence of water they explain as necessary, first, for keeping the temperature of the reaction sufficiently low; secondly, for condensing the sulphuric acid as it forms. They also observed in the process the production of white star-shaped crystals, which on contact with water gave out nitre-gas with a strong evolution of heat, and they already suspected that this compound had a prominent share in the acid-forming process.

H. Davy showed, in 1812, that the presence of water is absolutely necessary (Berzelius, *Lehrbuch*, i. p. 471), because in the dry state the gases do not react upon each other; but a small quantity of water added to the mixture of sulphur dioxide and nitrous vapours causes the formation of the crystals observed by Clément and Désormes. Davy, therefore, considered that body an intermediate link indispensable for the formation of sulphuric acid; with our present notation we should express his opinion in this way:—

$$\begin{array}{rlcl} \text{I.} & 2SO_2 + 3NO_2 & + H_2O & = 2SO_2(OH)(ONO) + NO; \\ \text{II.} & 2SO_2(OH)(ONO) & + H_2O & = 2SO_2(OH)_2 + NO_2 + NO; \\ \text{III.} & 2NO + 2O & & = 2NO_2. \end{array}$$

Therefore we commence with $3NO_2$; and we recover of this

$1NO_2$ in the equation II., $2NO_2$ in the equation III., in order to begin the process over again.

This opinion has been accepted by many other chemists, for instance La Prévostaye (*Ann. Chim. Phys.*, lxxiii. p. 326), Gmelin also adopted it (*Handbuch*, 5th ed. i. p. 875).

An *apparently* simpler explanation of the vitriol-chamber process was given by Berzelius (*Lehrbuch der Chemie*, Woehler's translation, 4th ed. 1835, vol. ii. p. 12). He believes the formation of chamber-crystals to be not a necessary intermediate process, but only an exceptional case happening in some parts of the chamber where steam is wanting. The process proper, according to him, is the transference of oxygen from "nitrous acid" to sulphur dioxide (and water), producing sulphuric acid and nitric oxide, from which, by means of oxygen, nitrous acid is regenerated.

We should have to express that theory in our present notation by the following equations:

$$(1)\ SO_2+N_2O_3+H_2O = H_2SO_4+2NO;$$
$$(2)\ 2NO+O = N_2O_3.$$

But I have shown (*Ber.*, 1888, p. 3225) that Berzelius, as was natural in those days, made no sharp distinction between N_2O_3 and N_2O_4, and evidently by "nitrous acid" often means N_2O_4. It is also an important fact that in his *Jahresber.* for 1844, when the difference between N_2O_3 and N_2O_4 had become clearer, he distinctly states (p. 62) that N_2O_4 is formed when NO meets a sufficient quantity of oxygen or atmospheric air, whilst with an excess of NO, that is, in case of a deficiency of oxygen, N_2O_3 is formed, together with some N_2O_4. In fact most subsequent writers have not introduced nitrous anhydride, but *nitrogen peroxide* into the explanation of the chamber-process, starting from the indubitable fact that in ordinary laboratory experiments nitric oxide with an excess of oxygen forms almost entirely, or perhaps even exclusively, nitrogen peroxide, and tacitly assuming (without any proof of ever having attempted to detect its presence) that nitrogen peroxide was the oxide of nitrogen prevailing in vitriol-chambers; also overlooking that the above-mentioned laboratory fact is entirely modified by the presence of other substances in the vitriol-chamber. Thus it came to pass that the following equations were generally held to express the vitriol-chamber process:—

$$(3)\ SO_2+NO_2+H_2O=H_2SO_4+NO;$$
$$(4)\ NO+O=NO_2.^1$$

The great simplicity of this expression seemed to be its recommendation, but it was overlooked that in nature the simplest explanation is very often *not* the expression of truth.

Even long after Berzelius no sharp distinction was made between the equations (1)+(2) and (3)+(4); probably most chemists tacitly assumed, as was explicitly done by some, that the vitriol-chambers contained a mixture of N_2O_3 and N_2O_4, both of which acted as oxygen carriers upon SO_2, and this was generally meant when speaking of the "theory of Berzelius," which was certainly accepted by very many chemists.

For some time another theory, that of Peligot, published in 1844 (*Ann. Chim. Phys.* (3), xii. p. 263), contested the palm with it, and was accepted, more especially in France, for a long time; even Kolb (*Études sur la Fabrication de l'Acide sulfurique*, Lille, 1865, p. 22) adhered to it; and so did Pelouze and Frémy (*Traité de Chimie*, 2nd edition, i. p. 398).

Peligot, like Berzelius, denied that the chamber-crystals had an essential share in the formation of sulphuric acid, or that they appeared at all in the regular process, either in a solid form or in solution. He attributes the oxidation of the sulphur dioxide within the lead chamber exclusively to nitric acid, not to the lower oxides of nitrogen. The water is added to decompose the hyponitric acid formed from nitric oxide and atmospheric oxygen, or the nitrous acid formed at the same time, into nitric oxide and [hydrated] nitric acid, and thus to regenerate the only oxidising agent acting in this process, viz. nitric acid. In watery solution, he says, no nitrous acid exists [which is altogether wrong]; from a mixture of nitric oxide and atmospheric air not N_2O_3, but only N_2O_4 is formed. These opinions will be made clearer by the following equations (rendered into modern symbols):—

$$\text{I. } SO_2+2NO_2.OH=SO_2(OH)_2+N_2O_4;$$
$$\text{II. } 2N_2O_4+H_2O=N_2O_3+2NO_2.OH;$$
$$\text{III. } 3N_2O_3+H_2O=4NO+2NO_2.OH;$$
$$\text{IV. } 2NO+2O=N_2O_4.$$

---

[1] Here, as in all other instances, we shall use the symbols N_2O_4 and NO_2 as interchangeable according to convenience of expression.

The experiments upon which Peligot founded his theory certainly proved that *concentrated* nitric acid oxidises sulphur dioxide even at the ordinary temperature, nitrogen peroxide being formed. But sulphur dioxide acts with more difficulty on *dilute* nitric acid, and only with the aid of heat, nitric oxide being formed. Weber points out that Peligot's experiments do *not* prove that nitric acid of that degree of dilution which, according to his own theory, must exist in the lead chambers, viz. only 2 per cent. $HNO_3+98\ H_2O$, at the temperature prevailing there, is really decomposed by sulphur dioxide. On the contrary, according to Weber's observations, nitric acid of such a degree of dilution is not at all changed when cold by sulphur dioxide; there is no appreciable action between them below 80° C., a temperature which, in normal work, is not prevalent in the lead chambers.

The researches of R. Weber in 1866 and 1867 (Poggendorff's *Annalen*, cxxvii. p. 543, and cxxx. p. 329) proved the complete futility, in all respects, of Peligot's theory, and greatly contributed towards elucidating the process within the lead chamber.[1]

He showed that, whilst dilute nitric acid has next to no action on sulphur dioxide at the ordinary temperature, there is a strong action between SO_2 and water which has absorbed the vapour of nitrogen peroxide, or if such water is added to the same dilute nitric acid which at first showed no action, or, more simply, if, instead of pure nitric acid, fuming nitric acid strongly diluted with water be used. Accordingly, the nitrous acid generated by the contact of nitrogen peroxide and water oxidises the sulphur dioxide much more readily than nitric acid does; nitrous acid is therefore undoubtedly the primary cause of the reaction for the formation of sulphuric acid when moist air meets sulphur dioxide and the vapour of nitrogen peroxide. The nitric acid which is formed on the decomposition of N_2O_4 by water remains undecomposed by SO_2 *if much water is present.* Under certain circumstances, however, as will be shown below, the nitric acid is decomposed as well.

For the chamber-process the behaviour of N_2O_4 and N_2O_3 towards sulphuric acid of various degrees of dilution with water must also be taken into account, as those gases come into contact with such acids, both in the shape of minute drops suspended in the atmosphere of the chamber and in the stock collected at the bottom. According to their degree of dilution the sulphuric acids contain nitrososulphuric acid (chamber-crystals), free N_2O_4 or N_2O_3, as has been explained in detail on pp. 332 *et seq.*; but all these liquids, when their density is much higher than that of ordinary chamber-acid, are rapidly decomposed by sulphur dioxide, sulphuric acid being formed. The decomposition of the absorbed vapours by means of water for the purpose of forming nitric acid, is therefore quite unnecessary and improbable; but the water must serve for forming the hydrate SO_4H_2, and therefore only in its presence can SO_2 be promptly oxidised by N_2O_3.

---

[1] Some parts of Weber's as well as of Winkler's work have been noticed in Chapter III. pp. 340 *et seq.*

It is of importance in practice that moderately concentrated mixtures containing nitric acid are more easily decomposed by sulphur dioxide than highly concentrated ones. When nitrous acid is dissolved in the pure hydrate SO_4H_2, or even in ordinary vitriol of 170° Tw., sulphur dioxide does not act upon it at all, or at least very incompletely.

When operating with mixtures of nitric acid with *dilute* sulphuric acid of varying concentration, Weber found that in a mixture of pure nitric acid of 1·25 sp. gr. with sulphuric acid of 70° Tw. the nitric acid is not decomposed by sulphur dioxide in the cold, but quickly on being heated, with evolution of nitric oxide; in the case of stronger acids (from 77° Tw. upwards) the decomposition begins in the cold, and the liquid then contains nitrous acid. Evidently the sulphur dioxide first produces nitrous acid in those mixtures, which is proved by their colour and by their action on potassium iodide; and in the *second* stage the nitrous acid yields up oxygen direct to the sulphur dioxide, without being compelled, as Peligot assumed, to be redecomposed into nitric acid and nitric oxide—a preposterous assumption. Thus even dilute nitric acid, brought into contact with moderately strong sulphuric acid, may be useful for the chamber-process, as in that case it yields up its water to the sulphuric acid, and in the concentrated state it is readily attacked by sulphur dioxide; this is just what takes place in the chamber.

According to Weber's theory, the following process takes place within the chambers:—The sulphur dioxide is oxidised, mainly by the oxygen of the nitrous acid, which thereby passes into nitric oxide; it does this, however, only when dissolved in water or in dilute sulphuric acid; and such a watery solution is formed either direct from free N_2O_3 or by the decomposition of N_2O_4. In the latter case, at the same time, nitric acid is formed, which can only be decomposed by the mediation of already formed sulphuric acid. The part played by the water has just been explained.

There is an agreement in many, but not in all, points between the opinions of Weber and those published almost simultaneously by Cl. Winkler (*Untersuchungen, etc.*, p. 20). Winkler also affirms the oxidation of sulphur dioxide by nitrous acid; but according to him the part played by nitrogen peroxide is more essential than that which Weber assigns to it. Winkler considers the latter to be formed principally by the action of air on nitric oxide; it then combines with sulphur dioxide and water to form nitrososulphuric acid, which sinks to the bottom in the shape of the well-known mist, here comes into contact with the dilute hot chamber-acid and dissolves in it, evolving gaseous N_2O_3, which oxidises a fresh quantity of sulphurous acid, thereby passing into NO, the latter beginning the process anew.

The fact that Weber points chiefly to N_2O_3, Winkler principally to N_2O_4, as the active agents in the chamber-process does not form a very essential difference in their views, as neither of them assumes either of these oxides to be formed exclusive of the other. A more fundamental difference is this, that Weber, like Berzelius, does not admit the intermediate formation of nitrososulphuric acid as an essential feature of the process, whilst Winkler does so, thus reverting to Davy's theory, which he merely develops in the light of modern knowledge, and more especially of his own investigations.

Formerly some writers objected to the theories hitherto stated, that there is a difficulty in assuming the simultaneous oxidation of nitric oxide and the reduction of higher oxides to NO. But this objection cannot be held as valid, and it would apply to any other theory ever brought forward for the chamber-process, or, for that matter, for any other process where an "intermedium" or "carrier" comes into play, and what would now be called a "catalytic" or "pseudocatalytic" process (see below). Although both processes undoubtedly take place at the same time, this may happen in the same chamber under different conditions: when in a certain part nitrous gas is reduced to nitric oxide, sulphur dioxide vanishes at that part, and the excess of oxygen present everywhere can now oxidise the nitric oxide again; by currents, diffusion, etc., fresh sulphur dioxide is brought in, and the process commences again. Besides, in any case the law of the action of masses comes into play in that part of the process where reversible reactions take place, *i.e.* the decomposition of nitrososulphuric acid by water, as we shall see later on.

When, in 1878, the first edition of this work was written, the question had not practically advanced beyond the labours of Weber and Winkler, both of whom relied on laboratory experiments, not on researches made with actually working vitriol-chambers. The composition of the gases in normally or irregularly working chambers was not even known. The colour of the gases precluded the assumption that in the chambers NO was the prevailing oxide of nitrogen, except perhaps in the first part of the system; it was also known that nitric acid did not make its appearance there except under very irregular conditions. But the choice still lay between N_2O_3 and N_2O_4 as the prevailing constituent of the "nitrous vapours" in the vitriol-chamber, and it was not known which of these might be the real oxygen carrier. I myself at that time thought I had good reasons for assuming that in a *normally* working chamber, where there is neither too much nor too little oxygen, the nitrous acid greatly predominates over the nitrogen peroxide.

A solid basis for a true theory of the vitriol-chamber process could only be formed by investigating the manufacturing process itself in all its stages, and, both as regards normal and irregular work, by an extended series of gas-analyses and other pertinent observations. The first and hitherto the only complete investigation of this kind was that made subsequently by myself in conjunction with Naef at the Uetikon works, near Zürich, to which allusion has already been made (*Chem. Ind.* 1884, pp. 5 to 19). The results of this investigation have not been shaken by any others carried out since, so far as the facts of the case are concerned; but the explanations at that time given by myself and by other chemists have had to be modified considerably, especially in consequence of the further experimental work conducted by me in 1885 (*J. Chem. Soc.*, xlvii. p. 465; *Ber.*, xviii. p. 1384; *cf.* other work done before and after, mentioned Chapter III. pp. 336 *et seq.*). I proved that in the *dry* state, and out of the reach of sulphuric acid, nitric oxide with an excess of oxygen combines to form nitrogen *peroxide* exclusively, or nearly so. If dry nitric oxide, being in excess, meets with an insufficient quantity of oxygen, a considerable amount of N_2O_3 is formed together with N_2O_4 (according to the view held at that time). In the presence of moisture, nitric oxide and excess of oxygen combine to form nothing but nitric acid. *Dilute* sulphuric acid (sp. gr. 1·405) acts on the whole like water, but a small quantity of nitrous acid is formed, as much as can exist in a stable solution in the acid (nitrososulphuric acid cannot exist in such dilute acid). Perhaps the most important observation, combined with others formerly made, was this:—If *strong* sulphuric acid is in presence of a large excess of oxygen, and nitric oxide is slowly passed into it, only that portion of NO which is in *immediate* contact with sulphuric acid, and so far as nitrososulphuric acid can be formed, is not oxidised beyond the state of N_2O_3 (as previously found by Winkler and myself); but all the gaseous molecules coming into contact with oxygen *outside* the acid, even immediately above it, behave like dry NO and excess of O generally—that is, they combine to form N_2O_4.

This last observation made it impossible to maintain, as had been done in the first edition of this work, and in some of my later papers, that the reason why the excess of O within the vitriol-chambers do not from the NO produce altogether NO_2, but N_2O_3 (or rather a gaseous mixture of approximately that composition) lies in the fact that there is a mist of sulphuric acid floating all over; for the liquid particles of sulphuric acid forming that mist are still at very great distances from one another relatively to the amount of molecules of NO and O present, and wherever the latter act upon one another otherwise than in immediate absolute contact with the acid, they will not yield N_2O_3, but N_2O_4.

Raschig (*Annalen*, ccxlviii. p. 135) asserted that nitric oxide, even when meeting a very large excess of oxygen, is not converted into N_2O_4, but into N_2O_3, provided that the oxygen is diluted with nitrogen, as in atmospheric air. But this assertion, which was already at that time opposed to the statements of all other chemists, was entirely disproved by my researches (*Berl. Ber.*, 1888, p. 3234), which showed that Raschig's experiments were badly conducted, and that NO is transformed into nitrogen peroxide by atmospheric air just as well as by pure oxygen.

The whole of Raschig's arguments and hypotheses are vitiated by the recognition of the fact that nitrogen trioxide, N_2O_3, does not exist in the gaseous form except in traces, as we have shown before (p. 332). Of course my own theory is also affected by the above fact. But, as I have shown in Chapter III. p. 333, that theory is altogether compatible with the light gained by more recent knowledge, since a mixture of $NO+NO_2$ behaves towards sulphuric acid exactly like N_2O_3.

Raschig's own theory of the vitriol-chamber process (*Annalen*, ccxli. p. 242), propounded at that time, assumed as an intermediary link the temporary formation of a compound which he calls "dihydroxylamine-sulphuric acid," of the formula $(OH)_2NSO_2OH$, but which nobody has seen, and whose preparation in the free state he himself did not expect to be possible. He assumes this compound to be formed when nitrous and sulphurous acid meet, but to be instantly decomposed with more nitrous acid into NO, SO_4H_2, and H_2O; NO is then again oxidised to nitrous acid, and the process begins anew.

I have shown (*Ber.*, 1888, pp. 67 and 3223) how unfounded are all the arguments adduced by Raschig for his view. A summary of the controversy was given by Hamburger in *J. Soc. Chem. Ind.*, 1889, p. 164.

Several facts have to be reconciled in any true theory of the lead-chamber process: 1st, the fact that the chambers contain at first a mixture of more than 1 mol. NO to 1 mol. NO_2, later on almost exactly equal molecules of NO and NO_2, but in regular work never any excess of NO_2 over this proportion, which excess we have in our former discussions called "free" nitrogen peroxide (Lunge and Naef's observations at Uetikon); 2nd, that NO and an excess of O combine to form N_2O_4, and only where NO and O meet at the same time sulphuric acid of sufficient concentration they form nitrous acid, but not in the free state, merely in the shape of $SO_2(OH)(ONO)$; NO and O, in the presence of H_2O and SO_2, may also form directly $SO_2(OH)(ONO)$. A new theory of the chamber-process, based on these fundamental and all other observed facts, had been clearly, although very briefly, indicated by myself in my before-mentioned paper of 1885 (*J. Chem. Soc.*, xlvii. p. 470), and it was further developed in subsequent papers, especially *Ber.*, 1888, pp. 67 and 3323.

The principal ideas of that theory were stated by me in 1885, as follows:—"*Sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitrososulphuric acid, which floats in the chamber as a mist; on meeting an excess of water, equally floating about as a mist* [probably mostly or all in the shape of very dilute sulphuric acid], *the nitrososulphuric acid splits up into sulphuric acid, which sinks to the bottom, and nitrogen trioxide, which begins to act anew. Hence it is not, as hitherto generally assumed, the nitric oxide,* NO, *but the nitrogen trioxide,* N_2O_3, *which acts as carrier of oxygen in the vitriol-chamber process.*" As mentioned later on, the formation of sulphuric acid is not brought about by alternate *oxidation* of NO to N_2O_3 or N_2O_4, and subsequent *reduction* of these compounds to NO, but by a *condensation* of nitrous acid with sulphur dioxide and oxygen into nitrososulphuric acid, and a subsequent splitting up of this compound by an excess of water, as represented by the following formulæ:

$$(1)\ SO_2 + NOOH + O = SO_2(OH)(ONO),$$

$$(2)\ SO_2(OH)(ONO) + H_2O = H_2SO_4 + NOOH.$$

At the same time, I pointed out that these reactions were or might be locally modified by special circumstances in different parts of the chamber, and this matter was treated in detail in my papers of 1888.

We see at once that that theory goes back to Davy's theory of 1814, subsequently upheld, among others, by L. Gmelin and Cl. Winkler, according to which the intermediate formation of nitrososulphuric acid (chamber-crystals) is a necessary link in the chamber-process. But my new theory removed the complication of those former views, and their partial contradictions to observed facts, by denying the necessity of a reduction to NO as an indispensable factor in the process, from which reduction would follow the formation of an excess of nitrogen peroxide in the chamber.[1] We will now follow up the new theory in detail and consider the modifications which the process suffers by local circumstances in certain parts of the chamber.

Let us remember that the gases of a normally working chamber contain at first an excess of NO, further on and right to the end only an equivalent mixture of $NO+NO_2$, equal to N_2O_3. An excess of nitrogen peroxide over that proportion is found only in case of irregular work, when by sending an unnecessary excess of nitrous gases into the chambers the formation of sulphuric acid has been finished too early, and the last part of the chambers contains extremely little SO_2; in this case only free NO_2 is there found. A greater or smaller excess of oxygen is without any influence on the question whether $NO+NO_2$ or more NO_2 is formed.

Although we now know that N_2O_3, when liberated from its combination with sulphuric acid, immediately dissociates for the most part into $NO+NO_2$, a very small quantity of N_2O_3 remains as such and can enter into the above-stated reaction (1) (p. 997); and according to the law of mass-action immediately more $NO+NO_2$ recombines to form N_2O_3, so that no sensible quantity of NO has time to form with oxygen "free" nitrogen peroxide, as SO_2 is present everywhere and leads to the formation of SO_5NH.

The same compound will be formed according to equation (9) (see p. 1001) by SO_2 from any locally existing free NO_2.

The orange vapours filling the chambers consist of a mixture of NO and NO_2, the former being in excess in the light-coloured front part of the chamber-system, whilst later on the proportion (as shown by analysis) is almost exactly $=NO+NO_2$, which constantly again acts with H_2O, SO_2, and O to form SO_5NH, and is re-formed from the latter by the action of more H_2O, as shown by the equations:

$$\begin{array}{lll}
(1\ b) & SO_2+NOOH+O & =SO_5NH, \\
(2\ b) & 2SO_5NH+H_2O & =2H_2SO_4+N_2O_3, \\
(3\ b) & N_2O_3+H_2O & =2NOOH
\end{array}$$

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[1] By "free" nitrogen peroxide I mean any excess of NO_2 over the proportion required to form N_2O_3 with NO, here as well as in all other places.

or else:

$$(1\ c)\quad 2SO_3 + NO + NO_2 + O_2 + H_2O = 2SO_5NH,$$
$$(2\ c)\quad 2SO_5NH + H_2O = 2H_2SO_4 + NO + NO_2.$$

The reactions formerly assumed by Berzelius (with the qualification expressed on p. 989), R. Weber, myself, and although but indirectly, by Raschig, namely:

$$(3)\quad SO_2 + N_2O_3 + H_2O = H_2SO_4 + NO,$$
$$(4)\quad 2NO + O = N_2O_3,$$

cannot represent the chamber-process: for, firstly, in this case there would be everywhere in the chambers, up to the end, a large number of molecules of NO together with N_2O_3, which is not the case; and secondly, the reaction (4) does not take place at all except in *immediate* contact with (strong) sulphuric acid; but in contact with sulphuric acid there is no free N_2O formed, but SO_5NH, and we are thus forcibly brought back to reactions (1) or to reaction (7), mentioned below. If in the back parts of the chambers NO (more than required for the formula $NO + NO_2$) existed to any extent in the free state for any appreciable length of time, it would there be oxidised into nitrogen peroxide, and this in contact with either water or sulphuric acid will form nitric acid, which should be found, at least to a great extent, unchanged, as it is a sufficiently stable compound in that part of the chamber, where there is far too little SO_2 and too low a temperature to reduce much HNO_3. But since HNO_3 is *not* found in normal working back-chambers, nor in the Gay-Lussac acid, *any theory based on the regular reduction of nitrous vapours down to nitric oxide*, NO, *cannot be accepted as true*, as it involves the formation of "free" N_2O_4, and subsequently that of HNO_3.

It is important for our theory to notice that sulphuric acid, such as found in the chambers, certainly dissolves very sensible quantities of SO_5NH, and indeed all the "drips" and even the bottom acid of the back-chambers testify to this. But this solubility, or, as it is better expressed, the stability, of SO_5NH is greatly diminished both by a higher temperature and by dilution of the acid (*cf.* pp. 339 *et seq.*), and this behaviour is indeed the foundation of all former processes for denitrating nitrous vitriol (pp. 846 *et seq.*). In the vitriol-chambers the temperature is much above that of ordinary air; the second condition is also fulfilled, for as soon as the SO_5NH formed in one place, and floating about in the shape of a fine mist, meets with particles of water or of dilute sulphuric acid floating about as well, it must suffer decomposition according to equation (2), p. 999, so that sulphuric acid and nitrous acid are formed. Only those portions of nitrosqsulphuric acid which are in immediate contact with the bottom-acid will be dissolved by this, and will thus be temporarily withdrawn from decomposition; but this takes place to a somewhat greater extent only in the back chambers, whilst in the front chamber, where both the higher temperature and the excess of SO_2 act as denitrating agents, the bottom-acid shows little or sometimes even no "nitre."

The views hitherto brought forward do not, however, explain the whole of the vitriol-chamber process; they must be modified for the first part of the chambers, which is filled with opaque white clouds, and where Lunge and Naef have proved the existence of much NO in excess above the proportion $NO+NO_2$. The temperature is highest and the formation of acid most vivid in this region. It is not in itself impossible that here the following direct reactions take place:

$$(5)\quad SO_2+NO_2+H_2O=H_2SO_4+NO,$$
$$(6)\quad SO_2+2NOOH=H_2SO_4+2NO,$$

which would explain the occurrence of NO. The latter, when meeting SO_2 and O, both present here in large excess, forms directly nitrososulphuric acid:

$$(7)\quad 2SO+2NO+3O+H_2O=2SO_5NH.$$

Locally, where water is in excess, nitric acid will be formed, but here, where this acid is in the state of vapour, and where it at once meets an excess of SO_2, it is instantly reduced by the reaction:

$$(8)\quad SO_2+HNO_3=SO_5NH.$$

In fact in this first part of the chambers the conditions are still altogether analogous to those prevailing in the immediately preceding Glover tower, and are entirely different from those occurring in the back part of the chambers, where the temperature is lower and there is very much less SO_2 present. In the front part the NO finds such an excess of SO_2, O, and H_2O, that the formation of N_2O_4 is either altogether precluded, or if any small quantity of it is locally formed it must be instantly absorbed again, according to equation:

$$(9)\quad 2SO_2 + N_2O_3 + O + H_2O = 2SO_5NH.$$

In the first part of the chamber system "free" nitrogen peroxide does not and cannot exist in appreciable quantities, and therefore the formation of sulphuric acid according to equation (5) *does not play any, or no appreciable, part.* Equation (6) is practically on the same lines.

This does not yet explain why there is in fact a large excess of NO present in the first part of the chambers. We seek this explanation in a secondary reaction which under the existing conditions is bound to occur, viz.:

$$(10)\quad 2SO_5NH + SO_2 + 2H_2O = 3SO_4H_2 + 2NO.$$

This is, of course, precisely similar to that which takes place in the immediately preceding space, that is, in the Glover, the conditions being identical in both cases: presence of large quantities of nitrososulphuric acid, of SO_2, of H_2O, and an even higher temperature than near the top of the Glover tower, where the inflowing acid has a cooling action. Thus more NO is formed than can be at once taken up by reaction (7).

The general results arrived at are as follows:—The *principal reactions* conducing to the formation of sulphuric acid in the vitriol-chambers are, the *formation of nitrososulphuric acid* from sulphur dioxide, oxygen, and nitrous acid (eq. 1), and its subsequent *decomposition* when meeting with water or dilute sulphuric acid (eq. 2). Whether N_2O_3 exists for an appreciable time as undecomposed vapour or not, is not a decisive point in this case, as we may introduce the hydrate NOOH, and as the components $NO + NO_2$ act just as N_2O_3. Besides this principal reaction, another set of reactions take place in the first part of the chambers, where the nitrososulphuric acid is partially denitrated by the excess of sulphur dioxide (eq. 10), and the nitric oxide thus formed combines directly with SO_2, O, and H_2O to reform SO_5NH (eq. 7). All the other reactions enumerated above either play no part whatever, or only an insignificant part in the chamber-process, and "free" nitrogen peroxide especially does not occur at all in normally working chambers.

The mutual action of the agents meeting in the vitriol-chambers partly belongs to the class of *reversible reactions*, whose direction in one sense or another is determined by the "action of mass," one or several of the components being in excess. The direct reaction $SO_2 + O + H_2O = H_2SO_4$ is *not* reversible at the maximum temperature of the lead chambers, but some of the intermediate reactions are. If oxygen or nitrous acid is in excess, the condensing reactions (1) and (7) prevail, and thus the formation of nitrososulphuric acid is induced; but if sulphur dioxide is present even only in *relative* excess, the denitrating reaction (10) prevails, and NO is split off. This does no harm in the first part of the chambers, where there is time for the NO to enter into the condensing reaction (7); but if it happens in the back part, the NO is lost, as it is not retained in the Gay-Lussac tower and escapes into the air. Another reversible reaction is that between sulphuric acid, nitrous acid, and water; where the sulphuric acid is in excess, we have:

$$H_2SO_4 + NOOH = SO_5NH + H_2O;$$

where, on the other hand, water is in excess, we have:

$$SO_5NH + H_2O = H_2SO_4 + NOOH.$$

Nothing is more certain in the manufacture of sulphuric acid than that the process of converting sulphur dioxide into sulphuric acid takes place in a regular way only by the action of a large excess of oxygen and of nitrous vapours; in case of a smaller excess of these agents sulphur dioxide escapes into the air. Both theory and practice show that even with the greatest excess of oxygen it is not possible to effect an absolutely complete oxidation of SO_2; it is generally agreed that the best practical limit is attained if the exit-gases contain 0·5 per cent. of the sulphur originally employed in the shape of SO_2. The rate at which the formation of sulphuric acid takes place under the given conditions of a certain excess of oxygen and of nitrous vapours has been mentioned before (pp. 958 *et seq.*) as observed experimentally. It has also been mathematically deduced, first by Hurter (*J. Soc. Chem. Ind.*, 1882, p. 52), afterwards by Sorel (in his frequently quoted paper); but their very hypothetical calculations lay claim to interest mostly on the ground that they are in general accordance with previously observed facts, and we must refer those interested in them to the originals.[1] Both authors also represent the normal working of the chambers by curves, with which Hurter compares the practical results of Mactear, and Sorel those of Lunge and Naef (which were not published at the time of Hurter's theoretical research).

We have previously (p. 964) compared Hurter's curves with Lunge and Naef's conclusions; in this place we will give the diagram in which Sorel represents the process (Fig. 350), both by his theoretical curves (drawn in full lines)—the upper one representing a loss of 0·5, the lower a loss of 24 per cent. of sulphur—and the results obtained by Lunge and Naef (in dotted lines). I have already (pp. 964 and 965) pointed out that whilst on the whole the rate of formation of the acid is in agreement with the theoretical curves, there are distinct breaks corresponding to the points where the gases leave one chamber to enter the next, and we have to some extent gone into the explanation of this phenomenon. But it is now time to give Sorel's explanation, which, although in full agreement with my theory of the vitriol-chamber process, amplifies it by specifying more distinctly the conditions under which either the first or the second of the main reactions,

$$(1)\quad SO_2 + NOOH + O = SO_5NH,$$
$$(2)\quad SO_5NH + H_2O = H_2SO_4 + NOOH,$$

takes place.

In an inert atmosphere nitrososulphuric acid will give up more or less N_2O_3, according to the concentration of the sulphuric acid, to the quantity of nitrous (or nitrososulphuric) acid, and to the temperature. If a certain quantity of N_2O_3 is removed from the surrounding gases, either directly or by reduction to NO, the acid will yield up more N_2O_3; if, on the other hand, the surrounding atmosphere becomes richer in N_2O_3 by oxidation of NO, the acid will again take up some N_2O_3. The tension of N_2O_3 in its solution in H_2SO_4 is increased by a rise of temperature, but much more by diluting the acid.

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[1] Sorel (*Fabr. de l'Ac. sulf.* p. 566) maintains that the first proposition of Hurter's is self-evident, but that the remaining propositions are mathematically untenable; moreover, that some of Hurter's conclusions, drawn from his mathematical reasoning, are partly contrary to experience. So much is certain, that practice has not profited in any respect whatever from his theory.

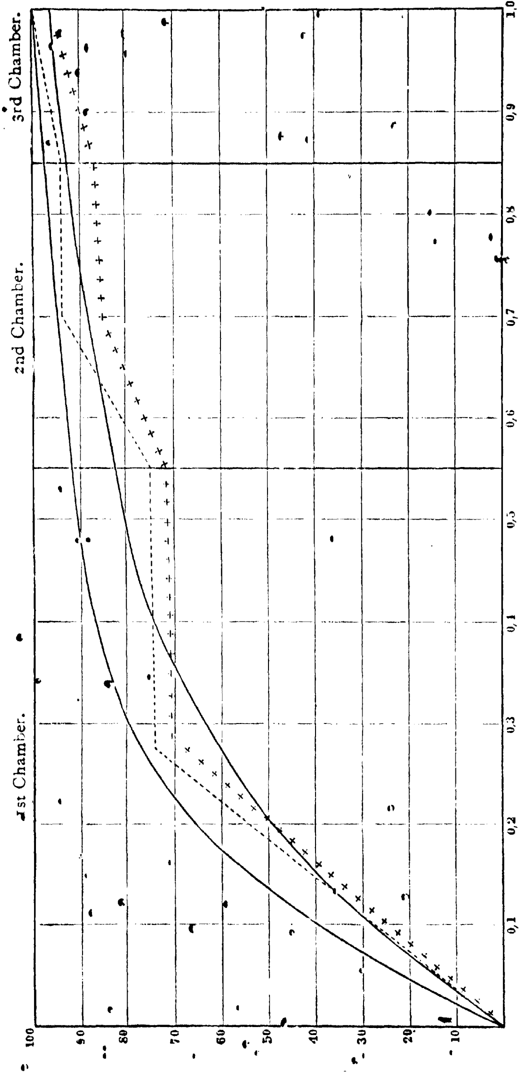
3rd Chamber.
2nd Chamber.
1st Chamber.
100
90
80
70
60
50
40
30
20
10
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,00

FIG. 350.

If, therefore, there exist in an atmosphere containing a certain quantity of N_2O_3, two solutions of N_2O_3 in sulphuric acid, one of them in concentrated, the other in dilute sulphuric acid, the former will enrich itself in N_2O_3 at the expense of the latter, even if it be to a certain extent hotter than the latter. Even the presence of SO_2 does not prevent the solution of N_2O_3 in sufficiently concentrated acid, provided that oxygen is present in excess and that the tension of the N_2O_3 (actually present or possible to be formed from NO and O) is greater than that of the acid in question. On the other hand, the SO_2 will decompose (*i.e.* denitrate) the acid if the outer tension of N_2O_3 is less than that of the acid, or on diluting the latter, or on raising the temperature. [These are indisputable facts, well known before Sorel, but very clearly put by him with the addition of bringing in the "tension" of N_2O_3, about which he could not have known very much in detail, and which, in the light of modern theories, we should partly or entirely replace by the mass-action of the vapours. Much more material for deciding these questions has been furnished by my own and my assistants' investigations, pp. 344 *et seq.*]

Sorel goes on as follows. We will, for instance, assume a certain definite quantity of acid of 57° Bé. (= 130°·4 Tw.), containing so much N_2O_3 that for a specified temperature the equilibrium with the surrounding gaseous mixture is established. This acid hovers as a mist in the gaseous mass. Suppose a certain volume of this gaseous mass is cooled down, the pressure remaining the same; then part of the aqueous vapour contained in the gaseous mixture will be precipitated in a liquid form and will dilute the acid. The acid will thus become incapable of withdrawing all its N_2O_3 from the influence of the SO_2 present; some NO will be formed, but also some H_2SO_4, by which the acid becomes more concentrated. If now the gaseous mass is brought back to the former, higher, temperature, the acid must, in accordance with the rise of temperature, yield up aqueous vapour, till it has again attained the density = 57° Bé., at which it once more fixes NO and O in the shape of N_2O_3.

Leaving out of consideration the secondary reactions, Sorel, like myself, regards the intermediate formation of nitrososulphuric acid (the fixation of oxygen upon sulphur dioxide by means of nitrous acid) as one of the principal reactions, followed by the decomposition of that compound, by dilution with water into sulphuric acid and nitrous acid.

The principal cause for determining the reaction in this or that sense is a *change of temperature*. We have seen before (p. 941) that the temperature near the leaden walls of the chamber is considerably less than that of the inner parts; therefore the gases must assume a quick rotation round a nearly horizontal axis, and each minute drop of acid, according to the change of vapour-tensions, must first be concentrated in the central portion and then be diluted again near the walls. Suppose we have a chamber-acid of 116° Tw. or 67 per cent. H_2SO_4. If, as was the case in a special experiment, the temperature next to the walls is = 75°, that in centre = 90°, the vapour-tension of 67 per cent. acid next to the wall will be = 27 mm. (*cf.* the table, p. 312); and since the acid hovering in the centre must have the same vapour-tension, but the higher temperature of 90°, its concentration (according to the same table) must be = 73 per cent. H_2SO_4 or = 130°·4 Tw. If, for instance, the acid near the wall had contained only 64 per cent. H_2SO_4, its vapour-tension would have been = 37·4 mm., and the hotter acid in the centre would at equal tension have contained 71 per cent. = 126° Tw. A number of observations made by Sorel at working-chambers show that the above-supposed differences do exist, which proves that the assumption of an equal vapour-tension all over the chamber is correct, and consequently also the assumption that regularly the concentration of the acid is greater near the centre than near the walls, where the cooling action of the air is at play. But as the greater concentration of the acid favours the fixation of nitrous vapours by SO_2 and O, in the shape of SO_5NH, and the greater dilution the decomposition of this compound into H_2SO_4 and N_2O_3, it follows that the formation of SO_5NH takes place chiefly in the centre, and that of real H_2SO_4 principally near the walls. The neighbourhood of the walls thus increases the production, as the cooling brings about the condensation of water, the dilution of the nitrous acid, and its decomposition into H_2SO_4 and N_2O_3. To a smaller extent this is also effected by the neighbourhood of the acid layer at the bottom, which is both cooler and more dilute than the acid floating about in the centre. All this is indirectly, but certainly, proved by the fact that a few centimètres from the wall, where the formation of H_2SO_4 must be strongest, and equally a little above the bottom acid, the greater intensity of the reactions is manifested by a rise of temperature.

As the gaseous current moves nearer the end of the chamber it becomes poorer in SO_2, and the reactions are therefore less intense. Moreover, observation shows that the temperature in the second half of the chamber hardly sinks at all in the centre, and but 2° near the walls. Less H_2SO_4 being made in this part, the acid in the centre is more dilute, and less able to fix N_2O_3 and SO_2 in the shape of SO_5NH, and that at a time when the smaller quantity of SO_2 anyhow makes this reaction more difficult. This, according to Sorel, explains the almost total cessation of the reactions in the back part of the first chamber, observed by Lunge and Naef; and it also explains the revival of the process in the second chamber observed by them, as the gases are *cooled* near the end walls of the chambers and in the connecting-pipe to the extent of 20° or 30° C. In fact a chamber exposed on the north side to the free air, and on the south side to the radiation from a second chamber, made at the north wall 2½ times more acid 3° Tw. stronger than at the south wall.

There must be a close connection between the temperature at the chamber-wall, the nitrous-acid tension, the intensity of the reactions at any given point, and the outside temperature. For every description of chambers, every special place in them, and every rate of manufacture, a certain temperature must be the most favourable—that which causes neither too much nor too little vapour-tension under the given circumstances. Both when the temperature is too high or when it is too low more nitre is used than under normal conditions [the damage done by too low a temperature is doubtful; *cf.* the Freiberg experiences, p. 939]. In the case of the "intensive" style of working, where the temperature is higher to begin with, any rise of the outside temperature makes less difference. Many manufacturers have adopted this high-pressure style (brought about by a very large supply of nitre, by means of ample Gay-Lussac and Glover space, *cf.* pp. 639 *et seq.*), where the draught is better and the cost of plant less; but this can only be done with medium-sized chambers, as otherwise the heat rises too much at the commencement.

We see how important, in Sorel's view, is the part played by the division of the total chamber-space into several chambers. We cannot doubt that in reality the cooling-action of the chamber-walls and ends and of the connecting-pipes is very important. But Sorel does *not* explain why, according to his own showing, the chamber temperature sinks very little in the second half, and very little acid is made there, although the surface of lead on this part of the two long sides and the roof is very much larger than on the two ends and the connecting-pipes taken together.

This seems to prove that the cooling is nothing like the *all*-important factor assumed by Sorel, and that the more intimate mixture of gaseous and liquid particles in the connecting pipes and the shock against the solid surfaces which brings about a condensation of the particles of mist to larger drops, where the *liquid* substances meet and react upon each other, must be equally acknowledged as potent factors for explaining the anomaly exhibited in the curves, Figs. 338 and 339, p. 964. In my own proposals for modifying the chamber system, as explained on pp. 657 *et seq.*, all the influences for reviving the chamber-process are brought into action,—that of an intimate mixture, of the shock against solid surfaces, and of the dilution of the acid by water, which at the same time serves as a cooling agent; and we have also seen that many years' practice has now proved the efficiency of those proposals to which I had been led, firstly by the experiments made by myself with Naef on the Uetikon chambers, secondly by my theoretical views as they were gradually evolved from both factory and laboratory work.

Ostwald (at the Congress of Electrochemists in 1895 and the German Naturforscher-Versammlung in 1901; *Grundriss der Allgemeinen Chemie*, 3rd edition, p. 516) has pointed out that the nitrous vapours in the lead-chamber process act merely as catalysing agents, by greatly increasing the speed of the otherwise very slow and incomplete reaction: $SO_2+O \times H_2O = H_2SO_4$. Of course no objection can be made against extending the class of "catalytic processes," with which we must of necessity deal when speaking of the manufacture of sulphur trioxide in Chapter XI., so as to embrace the vitriol-chamber process as well. But, as I have shown in *Z. angew. Chem.*, 1902, pp. 148 *et seq.*, it would be a grave error if we imagined that we are *explaining* that (or any other) process by calling it "catalytic," or that by giving it that name we may detract from the minute investigation of the *intermediary reactions.* On the contrary, only the latter can lead up to a real "explanation" of the process, just as will be shown in Chapter XI. In the present case Ostwald's enunciation has caused some little mischief, as others (like Th. Meyer), on the alleged authority of that eminent theoretical chemist, believed they might neglect as unessential the intermediate reactions between the nitrogen oxides and the other substances present. Ostwald himself did *not* go so far, he simply said that the assumption of intermediate products is not suitable for all cases; but proof should be given that intermediate reactions in fact proceed more quickly than the direct reaction. *But in the present case this proof is abundantly afforded by the experience of many generations, and is constantly repeated by every teacher of chemistry.* While the formation of sulphuric acid by the direct action of SO_2 on air and water is notoriously an extremely slow and incomplete process (p. 987), every lecturer on chemistry shows the *instantaneous* formation of chamber crystals when the above reagents meet with nitrous vapours, and the equally *instantaneous* decomposition of these crystals when meeting an excess of water. I cannot conceive a more complete fulfilment of the condition demanded by Ostwald, and a more utter *deductio ad absurdum* of those who would henceforth consider the reactions of the nitrous vapours in the lead chambers as unimportant "by-reactions" whose study is not essential for arriving at a theory of the chamber-process.

Several subsequent papers on the theory of the vitriol-chamber process can be only briefly quoted.

Loew (*Z. angew. Chem.*, 1900, p. 338) tries to apply the law of the action of masses to the above process. But, as I have shown (*ibid.*, 1902, p. 146), he makes inadmissible simplifications and other erroneous assumptions which render his reasoning futile.

Th. Meyer (*ibid.*, 1901, p. 1245) makes an even much less successful attempt in the same direction. I have shown (*ibid.*, 1902, p. 147) that he has entirely misunderstood the law of the action of masses, and has, moreover, committed so many other grave mistakes that there is no occasion to discuss his paper here, the less so as he has entirely acknowledged the justice of my remarks (*ibid.*, 1902, p. 278).

The discussion as to the possibility of establishing a mathematical theory on the above lines has been continued, without any practical result, by Riedel (*ibid.*, 1902, p. 462), Lunge (*ibid.*, p. 581), Haagn (*ibid.*, p. 583), Riedel (*ibid.*, p. 858), Lunge (*ibid.*, p. 931), Keppeler (*ibid.*, p. 809).

Of much greater importance is the paper, which we shall now refer to, viz. Brode's, in *Z. angew. Chem.*, 1902, p. 1081. He broadly surveys the laws of chemical dynamics, and I shall give a short abstract of this paper, so far as it concerns our subject. Theoretically every reaction may be regarded as incomplete at any temperature, since our analytical methods will never be sufficiently exact to detect the minutest traces of unchanged substances. But practically we must regard those reactions as *complete* in which the products of one side of the equation cannot be altogether *detected* and in which the reaction proceeds entirely in the ratio of the equivalent weights. These reactions are denoted by the mark of equality =. *Incomplete* are those reactions which are *reversible*, and which are denoted by the mark $\rightleftarrows$ (van't Hoff). At ordinary temperatures, for instance, the reaction $2H_2+O_2=2H_2O$ is complete, at high temperatures, it is incomplete:

$$2H_2+O_2 \rightleftarrows 2H_2O.$$

Nearly all reactions are incomplete at high temperatures, and at extreme temperatures the reaction would be complete in the opposite direction:

$$2H_2O=2H_2+O_2.$$

If we enquire how far different reactions actually take place, that is, if we regard the position of equilibrium, we find enormous variations, which we ascribe to the difference of chemical affinities. We measure these by the "constant of equilibrium," which, according to the law of the action of masses, has the following meaning:—For every reaction at constant temperatures the product of the concentrations of the reacting substances on one side of the equation, divided by the product of the concentrations of the substances on the other side, possesses a constant value, if we state the concentration in "moles" (gram-molecules per litre). If two, three, or n molecules react at the same time, in lieu of the simple concentrations the second, third, or nth power must be assumed. The constants are therefore independent of the concentration and remain unchanged for every reaction at certain temperatures. In the case of incomplete reactions their order of magnitude does not differ very much from unity; in the case of complete reactions their value approaches zero. The law of the action of masses admits of computing the shifting of concentrations consequent upon adding an excess of one of the components to a mixture in the state of equilibrium. If, for instance, in the reaction $c_1 + c_2 \rightleftarrows c$ the three substances are at equilibrium, they are in the relation: $\frac{c_1 c_2}{c^2} = \text{const.}$ If we now add to c_2 another quantity $= a$, there will be a change of x molecules in the sense of using up somewhat more of the substance c_2; when the equilibrium is again reached, the concentration of the second component will not be $c_2 + a$, but $c_2 + a - x$, and the concentrations will fulfil the following conditions:

$$\frac{c_1 c_2}{c^2} = \text{const.} = \frac{(c_1 - x)(c_2 + a - x)}{(c + x)^2}.$$

This admits of computing the value of x. If one of the components is in great excess, the concentration of the other component can be reduced to a very small value.

Van't Hoff has shown how the reaction-constants can be quantitatively computed from the "heat-toning" of the reaction. From this follows further that on the shifting of the equilibrium a phenomenon sets in which opposes the shifting and partially undoes its effect; hence any shifting through an elevation of temperature will be combined with a reaction which *absorbs* heat, and *vice versâ;* at extreme temperatures only such reactions will occur which absorb heat (formation of CS_2, CaC_2, (NC – CN). By increasing the *pressure* those reactions are promoted which reduce the total number of molecules.

But the laws of chemical equilibrium enlighten us only upon the *final state* into which a reacting mixture enters and whereupon no further spontaneous change takes place; they do not state anything concerning the *velocity of reaction*, the factor of time not finding any place in thermodynamical equations. Concerning this subject we may establish the following specifications:—

1. With increasing concentration of the substances *vanishing* during the reaction, the reaction velocity g increases, and in *complete* reactions is proportional to the concentrations of the moles per litre; thus: $g=kc_1c_2$; k being a constant to be found by experiment for each reaction and each temperature. On the other hand, the concentration of the *newly formed* substances comes into play only in *incomplete* reactions. Here g is the difference of two opposite reactions; the newly formed substances c_1, c_2, causing a change in one direction, the vanishing substances c_3, c_4, a change in the opposite direction: $g=k_1c_1c_2-k_2c_3c_4$.

In the state of equilibrium $k_1c_1c_2=k_2c_3c_4$, hence $g=0$. The equilibrium-constant k is the quotient of the two opposite velocity constants $\frac{k_1}{k_2}$. When a substance does not react with one molecule, but with n molecules, properly speaking the concentration ought to be expressed in the nth power in the equation of velocity, but experiment has generally shown that lower powers must be assumed. If the reaction goes on step by step, only one of which requires sensible time, the others proceeding with extreme velocities, the total reaction must proceed with the velocity of the slow intermediate reaction.

2. The influence of *temperature* is always felt by an enormous *increase of velocity on raising the temperature.* Generally raising the temperature $n\times10°$ increases the velocity by $2{\cdot}5n$; for instance $30°=2{\cdot}5\times2{\cdot}5\times2{\cdot}5$. Thus a process which at 100° requires an hour, at 0° will take a year.

3. By means of *catalysers* the velocity may be increased to such an extent that a reaction which by itself has an infinitely small velocity (=0), after adding a certain substance, which remains unchanged during the reaction, is effected in an immeasurably short time. As *pure catalysis* we denote the cases where intermediate reactions are impossible or unlikely; as *pseudo-catalysis* (Wagner), those cases in which intermediate reactions are proved or probable. Neither kind of catalysers can shift the position of equilibrium, otherwise we should attain a *perpetuum mobile*. Catalysers cannot possibly influence

the free energy of a system; they merely influence the time of reaction. What causes the difference in velocity of various reactions is an entirely unsolved problem.

The application of the above to the theory of the formation of SO_3 from SO_2 and O will be referred to in the 11th Chapter. Here we consider merely how far we can apply the hitherto attained results of chemical dynamics to the lead-chamber process. Brode agrees with me in holding that in this process, where hydrated sulphuric acid is *practically completely* formed at a maximum temperature of 90°, the laws of chemical equilibrium cannot be applied. We can only think of applying the laws of the velocity of reactions. Elsewhere we always notice an increase of velocity with increasing temperatures; how, then, can a complete reaction have an *optimum* of temperature? The explanation is this: that the pseudo-catalytical action of the nitrogen oxides in the chamber is founded on two intermediate reactions of different velocity. In such cases the time required by the entire reaction always depends upon the slower of the intermediate reactions. Since in the lead chamber water is always present in the shape of mist, the process goes on in two phases, the liquid and the gaseous. With an increase of temperature more and more aqueous mist is changed into steam. But nitrososulphuric acid requires *liquid* water for its decomposition, so that with the decreasing concentration of the latter the velocity of one of the intermediate reactions must equally decrease. Moreover this reaction is incomplete with low concentrations of water. We have thus an interesting case of pseudo-catalysis. The direct reaction is practically not reversible, nor is the first of the intermediate reactions,[1] but the second of these (the decomposition of nitrososulphuric acid by water) is reversible. Consequently after some time nothing remains of the original SO_2, but part of the SO_5NH will remain undecomposed, since for practical reasons, sufficiently elucidated in the text of this chapter, it is not feasible to employ in the last chamber a sufficient excess of water to completely decompose the nitrososulphuric acid. Thus a considerable quantity of the latter must remain up to the last, and it would be removed with the inert nitrogen and oxygen if it were not retained by the Gay-Lussac tower. This theory has explained the reason of the fact, known to practical acid-makers for more than half a century, that there must be a large excess of nitrogen oxides in the last chamber if the conversion of SO_2 into H_2SO_4 is to be practically complete.

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[1] *Cf.* (p. 343) my observations as to the great stability of nitrososulphuric acid in the absence of water.

Since in the lead chamber, as in every heterogeneous process, the velocities of condensation and absorption also essentially influence the total velocity, the reactions in the chamber are very complicated and are not yet accessible to mathematical treatment; hence a dynamical theory of the formation of sulphuric acid in the lead chamber cannot yet be established.

In his excellent treatise *Die Elemente der chemischen Kinetik* (Wiesbaden, 1902), Bredig equally shows that the quantitative working out of the intermediate reactions in the lead-chamber process must be an extremely complicated problem of chemical kinetics which is not likely to be realised very soon. At the present time we must be content with my above-given demonstration, that there is an enormous difference in velocity between the direct oxidation of SO_2 by O and the intermediate reactions postulated by me, which cannot be reactions of secondary importance, since they always occur *immediately* and *quantitatively* whenever the components meet.

The preceding pages give an account of the state at which the theory of the lead-chamber process stood at the time of the publication of the last edition of this volume (in 1903). Since that time a great many further contributions have been made to this subject, of which we shall now give a succinct account.

A very important paper on the physical chemistry of the lead-chamber process is that published by Trautz (*Z. physik. Chem.*, xlvii. pp. 513 to 610, abstracted in *Chem. Centr.*, 1904, i. p. 1301). He declares the mode of action of the nitrogen oxides in the chamber to be still unexplained from the physico-chemical standpoint; he has made experiments for filling up the gaps, and gives a critical review both of his own results and of former attempts in that direction. There is still uncertainty as to the kind of nitrogen oxides prevailing in the chamber. The oxidation of SO_2, dissolved in water or dilute sulphuric acid, is extremely slow without the assistance of a catalyser. As such we must regard the oxidised nitrogen compounds: HNO_2, NO_2, NO, HNO_3 and $SO_2(OH)(ONO)$. The action of HNO_3 as a catalyser is extremely complicated. The author studied in detail the conditions of equilibrium between nitrososulphuric acid and mixtures of H_2SO_4 and water at various concentrations, the concentration within the limits of chamber-acids being of especially great influence on the stability of nitrososulphuric acid. That acid, when mixed with aqueous sulphuric acid at a temperature of 25°, on passing an indifferent gas through it, is decomposed all the more quickly the more water is present, giving off NO, with which some NO_2 is found, all the more the less water and the more sulphuric acid is present. Besides there is a formation of water and of nitric acid; all the less, the less water is present. Dilute solutions (about 0·5 mol. H_2SO_4) appear to be merely sursaturated solutions of nitric oxide, whilst in more concentrated solutions the chemical action of hydrolysis is superposed over the pure sursaturation. The action of NO on mixtures of HNO_3, H_2SO_4 and water was studied in detail in a very ingeniously constructed apparatus, in which the objectionable use of india-rubber connections was avoided by spiral glass springs. The absorption of NO takes place with unmeasurable rapidity, with or without H_2SO_4; the results cannot be theoretically treated according to the law of masses, on account of the high concentration and the unknown dissociation of the solutions. NO forms with $HNO_3 + H_2O + H_2SO_4$, nitrososulphuric acid and NO_2; the partial pressure of the latter increases with an increase of the concentration of H_2SO_4 up to a maximum; at very high concentrations of the acid (93 per cent.) it has no measurable value. At this concentration, besides nitrososulphuric acid, also nitrosodisulphonic acid, $NO(HSO_3)_2$, is formed, approximately in inverse proportion to the concentration of NO_2. Up to 52 per cent. H_2SO_4 the process is quickly reversible at all temperatures between 22° and 82°, also in 55 per cent. H_2SO_4 at 82°. The concentration of NO and HNO_2 quickly decreases with rising temperatures; on the change of the percentage of H_2SO_4 their concentrations are changed at a complicated ratio. An increase of pressure favours the formation of NO_2 at the expense of NO. SO_2 acts on nitrososulphuric acid also when this is dissolved in 95 per cent. H_2SO_4, especially when hot. By the addition of water to this solution there are formed, according to the quantity of the water, H_2SO_4 and the excess of SO_2, SO_2+NO, NO alone, $NO+NO_2$, $NO+NO_2+N_2O$. The reaction: $NO(SO_3H)_2 + 2NO_2SO_3H + 2H_2O = 3NO + 4H_2SO_4$ may also occur in the lead chambers; most quickly at the conditions of temperature and concentration prevailing therein. Together with the previous reaction: $2\ NO_2, SO_3H + 3SO_2 + 2H_2O = 2NO(SO_3H)_2 + H_2SO_4$, and this: $2NO + O_2 = 2NO_2$. Trautz considers it to be more likely to occur than the direct reaction or that of the products of hydrolysis of nitrososulphuric acid; that hydrolysis is not the most productive reaction of the system, since it can hardly occur in the Glover tower, where most of the sulphuric acid is produced in another way. Raschig's theory permits of deriving many of the really occurring reactions from the least number of properties of the substances present, but his most important reactions have not yet been proved to occur under the conditions prevailing in the lead chamber. Owing to the immeasurably great velocity of the reactions the question is still open which of these play the greatest part in the lead chamber; very likely reactions still unknown occur there, since the number of the possible products of condensation is very great. Some or all of the following reactions occur in the chambers:—

(1) $NO + NO_2 + H_2O = 2NO.OH$

(2) $2NO.OH + 2HSO_3H = 2NO.SO_3H + 2H_2O$
$= NO(SO_3H)_2 + NO + 2H_2O$

(3) $NO(SO_3H)_2 + 2NO.OH = 3NO + 2H_2SO_4$

(4) $2NO + O + 2H_2SO_4 = 2ONO.SO_3H + H_2O$

(5) $2ONO.SO_3H + 2H_2O + NO(SO_3H)_2 = 4H_2SO_4 + 3NO$

(6) $NO_2.SO_3H + H_2O = NO_2H + H_2SO_4$.

Divers (*J. Soc. Chem. Ind.*, 1904, pp. 1178 *et seq.*) tries to reconcile the views of Lunge and Raschig, by making them to be with some excrescences parts of a more comprehensive theory, according to which the production of sulphuric acid in the lead chamber is due to action going on between the liquid and the gaseous parts of the mist, brought about by the momentary intervention of the two catalytes: nitrososulphonic acid and nitrososulphuric acid, $ON.SO_3H$ and $ON.O.SO_3H$. The liquid particles of the mist, consisting of strong sulphuric acid holding nitrososulphuric acid in solution, continuously absorb SO_2 and oxygen, which by the catalytic action of the nitrososulphuric acid are converted into sulphuric acid as fast as they are absorbed. In the normal working of the process water is taken up in such quantity as serves to effect incipient hydrolysis of the nitrososulphuric acid into its constituent acids. Two molecules of SO_2 and one molecule of O_2 are absorbed simultaneously, for the reason that they find between themselves the radical of the catalyser, nitrosyl, one moment as nitrososulphuric acid, and the next moment as nitrososulphonic acid. Or, leaving out all mention of the radical, nitrosyl, but remembering that the substance of the same formula, nitric oxide, NO, plays no part, the catalyser is nitrososulphonic acid and nitrososulphuric acid alternately.

Raschig, in his first paper of 1904, principally defends his formerly published views against the objections made against them by Divers. He gives reasons for assuming that free sulphurous and nitrous acid combine almost exclusively in molecular proportions to form dihydroxylaminesulphonic acid, $(HO)_2NSO_3H$ or nitrososulphonic acid, $ONSO_3H$, which comes to the same thing. Only a very great excess of SO_2 leads to the formation of the second stage, $HON(SO_3H)_2$, or the third stage, $N(SO_3H)_3$. He specially worked at the question how the nitrososulphonic acid, primarily formed, is decomposed. N_2O only appears on heating, but there is a formation of nitroxyl, $O=N-H$, which on boiling decomposes completely into N_2O and H_2O. Free nitroxyl acts hardly at all on nitrous acid in aqueous solution, with or without addition of sulphuric acid. But the product of condensation between free nitrous acid and SO_2, which by itself has only a small reaction on further nitrous acid, behaves quite differently on the addition of sulphuric acid, the reaction then being as strong as in the lead chamber. By the action of atmospheric oxygen the nitrous acid is at once regenerated, so that large quantities of SO_2 are oxidised. The lead-chamber process may be represented by the following equations:—

$$1.\ ON.OH + SO_2 = ON.SO_2.OH$$

$$2.\ ON.SO_2.OH + ON.OH = 2NO + HO.SO_2.OH$$

$$3.\ 2NO + O + H_2O = 2HO.NO.$$

Lunge (*Z. angew. Chem.*, 1904, pp. 1659 *et seq.*) objects to Raschig's theory, that it involves the formation of large quantities of nitrogen protoxide, N_2O, in the lead chamber, which notoriously does not take place. Raschig, he says, discourses on his assumed nitrososulphonic acid and in many other compounds never met with in a lead chamber, but he entirely omits to mention two compounds, found in large quantities in the chambers, viz., nitrogen peroxide, NO_2, and nitrososulphuric acid, $ONO.SO_2.OH$, which, if Raschig's theory were right, would do great damage by locking up nitrogen in a useless form. Raschig's principal error is that he neglects the very first postulate of the law of the action of masses, viz., the action which the presence of an enormous amount of free oxygen must have in the action of SO_2 on nitrous acid. This excess of oxygen prevents even the temporary formation of nitrososulphonic acid, in lieu of which nitrososulphuric acid is formed, Raschig's third equation: $2NO+O+H_2O=2HO.NO$ is wrong, for NO with oxygen in excess and water is quantitatively transformed into HNO_3, as everybody knows. Only in the presence of and in direct contact with sufficient concentrated sulphuric acid the oxidation of NO does not proceed beyond the nitroso state, but no free nitrous acid, only nitrososulphuric acid is always formed, and that quantitatively.

Engler and Weissberg, "Kritische Studien über die Vorgänge bei der Autoxydation," 1904, pp. 157 *et seq.*, declare nitric oxide to be an "autoxydiser," bringing about the action of the lead chambers concurrently in two ways, viz.:—

(*a*) Directly by itself:

$$2NO+O \rightarrow N_2O_4;\ N_2O_4+SO_3H_2 \rightarrow \overset{\text{Nitrososulphuric acid}}{ON.OSO_3H} + \underset{\text{Nitrous acid}}{ON.OH}$$

(*b*) Indirectly, in presence of a fine spray of sulphuric acid:

$$2NO+2SO_4H_2+O_2 \rightarrow 2ON.OSO_3H+H_2O_2 \rightarrow H_2SO_3+H_2SO_4+H_2O.$$

In both cases half of the oxygen taken up is given up to the "acceptor," sulphurous acid, according to the general scheme for such half-way combinations of molecular oxygen:

(*a*) Directly:

$$\begin{array}{ccccccccc} \text{Autoxydiser} & & \text{Peroxide} & & \text{Acceptor} & & & & \\ A & +O_2\rightarrow & AO_2 & + & B & \rightarrow & AO & + & BO \\ \text{Nitrogen oxide} & \rightarrow & \text{Nitrogen peroxide} & & \text{Sulphurous acid} & & \text{Nitrous acid} & & \text{Nitrososulphuric acid} \end{array}$$

(*b*) Indirectly:

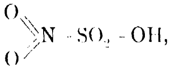
$$\begin{array}{ccccc} \text{Hydrogen} & \rightarrow & \text{Hydrogen peroxide} & \text{Sulphurous acid} & \text{Nitrososulphuric acid} & \text{Sulphuric acid.} \end{array}$$

The action in the chambers is rendered continuous by the specific property of nitrososulphuric acid, that is, of nitrous acid, at the conditions ruling in the chambers, to cause the re-formation of the autoxydiser, nitric oxide. The nitrogen peroxide formed at the same time is at the same time decomposed and deoxydised. The views of Engler and Weissberg, as they state, on the whole agree with that of Lunge, according to which nitrous acid, in the shape of nitrososulphuric acid, plays the part of catalyser and oxygen-carrier, but this is only a consequence of the special conditions offered in the lead chambers, where an energetic autoxydiser, NO, together with an excess of oxygen, acts on a ravenous acceptor, sulphurous acid, forming a compound which, under these circumstances, is stable, viz., nitrous acid in the form of nitrososulphuric acid.

The next paper is again by Raschig (*Z. angew. Chem.*, 1904, 1777). He does not believe that nitrososulphuric acid occurs in large quantities in the lead chambers, and that it is at all necessary for the formation of sulphuric acid and a necessary intermediate product. At most he takes it to be a constantly occurring by-product. He misses a proof for the assertion that the chamber-acid, which contains up to 0·03 per cent. N_2O_3, holds this in the shape of nitrososulphuric acid, and is not merely a simple solution of N_2O_3 in sulphuric acid. The occurrence of NH_3 in the chambers he takes to be exclusively explicable by his own theory on the formation of nitrososulphonic acid, which he holds to be certain, although that acid has not yet been obtained in the free state. He believes in the formation of real N_2O_3 from NO, whereas Lunge assumes in the chambers only a mechanical mixture of NO and NO_2, behaving like N_2O_3 against alkaline and acid reagents. As proof for his opinions he quotes experiments in which NO was mixed with an excess of atmospheric air and the gases were at once passed through decinormal soda-solution, which was at once retitrated and oxidised by $KMnO_4$. A few seconds after mixing the gases the mixture contained nothing but N_2O_3; twenty-five minutes later, almost exclusively NO_2. Hence NO is, by an excess of oxygen, instantaneously oxidised to N_2O_3, and this is only slowly further oxidised to NO_2. Further experiment with his "lead-chamber in a tumbler" corroborated that at first pure N_2O_3 is formed, only later on mixtures with HNO_3, but never beyond the proportion 1 : 1. Under the conditions of the lead chamber the only admissible equation is: $2NO + O = N_2O_3$; NO and N_2O_3 are the only nitrogen oxides normally occurring in the chambers. Only near the end of the chamber system, where the reactions have slackened down and only a few drops of dilute sulphuric acid are formed, ultimately a small quantity of NO_2 is found, a sign of "the weakness of old age."

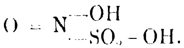
Lunge, in his reply (*Z. angew. Chem.*, 1905, pp. 60 *et seq.*), refers to the valuable paper of Trautz (cf. *suprà*, p. 1014), in which nitrososulphuric acid plays a principal part, the entirely hypothetical nitrososulphonic acid being set aside. "Even in Raschig's "lead-chamber in the tumbler" there is absolutely no proof for as much a transient formation of nitrososulphonic acid, let alone a proof for such a formation under lead-chamber conditions. The reduction of nitrites by sulphites to NH_3 is an old-established reaction in the manufacture of caustic soda, and therefore the occasional occurrence of traces of NH_3 in a lead chamber cannot have the importance attributed to it by Raschig, for if that chemist's theory were true, NH_3 must be found in large quantities in the chambers, as the final product of his chain of reactions." The absence of N_2O in the chambers also militates against Raschig's theory. Concerning the nitrososulphuric acid, whose presence in the chambers is denied by Raschig, Lunge gives figures from which it is seen that in the chamber to which his analysis refers, the acid contained 0·24 per cent. of nitrososulphuric acid, and the total acid of that chamber contained 2900 kg. of that compound. Lunge has for some time past withdrawn the opinion that sensible quantities of *free* N_2O_3 are present in the chambers. Raschig's last experiments are vitiated by his employing dilute caustic-soda solution as an absorbent for the gases; that dilute solution acts essentially like water and exhibits the well-known irregularities in the absorption of nitrogen oxides. Raschig's assertion that only half of the NO passes over into HNO_3, is vitiated by his employing such a large excess of water, and altogether he nearly always worked under conditions entirely different from those of the chambers. The formation of minute traces of free N_2O_3 in the chambers is quite possible, but that is very different from Raschig's assertion that N_2O_3 is the only product formed. Raschig's opinion that atmospheric oxygen, in consequence of the dilution with nitrogen, behaves quite differently against NO from pure oxygen, is refuted by experiments made by Lunge with Berl.

The next paper of Raschig's (*Z. angew. Chem.*, 1905, pp. 1281 *et seq.*) is summed up by himself as follows. (1) Nitric oxide, when meeting oxygen, is quickly converted into nitrogen trioxide, N_2O_3, and this is slowly further oxidised into nitrogen dioxide, NO_2 or N_2O_4. The times occupied by these two reactions are in the proportion of 1 : 100. [Raschig admits, on p. 1298, that this contention involves the invalidity of Avogadro's law, and he is bold enough to say that that law must be considered as being annihilated by his investigations. We must draw attention to the fact, that consequently those who assent to Raschig's views are thereby equally forced to deny the truth of Avogadro's law, which hitherto has been universally considered as one of the fundamental laws of modern chemistry!] (2) In the atmosphere of the lead chambers it takes three seconds to oxidise NO to N_2O_3, or four minutes to carry on the oxidation as far as NO_2. Since it is unlikely that in the lead chambers molecules of N_2O_3 and SO_2 meet so rarely that the former have time to oxidise into NO_2, it is necessary to assume that N_2O_3 is that oxide of nitrogen which reacts with SO_2 in the lead chamber. (3) The same conclusion is reached when observing the behaviour of N_2O_4 and N_2O_3 to SO_2 in the presence of water. N_2O_4 does not act at all on SO_2, but is dissolved as a mixture of HNO_3 and HNO_2, of which only the latter reacts with SO_2. N_2O_3, however, combines directly with SO_2. Hence 1 mol. N_2O_3 converts more SO_2 into H_2SO_4 than 1 mol. N_2O_4. (4) N_2O_3 or nitrous gases of similar composition are quickly and without causing errors dissolved by strong sulphuric acid, the analysis of which allows of ascertaining their composition. Caustic-soda solution does not so easily absorb N_2O_3, nor does water, and on entering into solution it does not form pure nitrite, but is partly split up into NO and NO_2, the former escaping unabsorbed and the latter dissolving to a molecular mixture of nitrite and nitrate. The error thus caused in analysing in the case of pure N_2O_3 amounts to 15 to 20 per cent.; in the presence of indifferent gases it is only 5 per cent. (5) N_2O_4 or nitrous gases of a similar composition dissolve easily and smoothly in caustic-soda solution, forming a molecular mixture of nitrite and nitrate, and can be accurately analysed in this way. In sulphuric acid N_2O_4 dissolves with difficulty and with loss of some oxygen. (6) The compound formed on dissolving N_2O_3 in sulphuric acid, known of old as "chamber-crystals," has not the constitution of nitrososulphuric acid, $O=N-O-SO_2-OH$, but it is nitrosulphonic acid,



$$O_2N-SO_2-OH,$$

in which the sulphur is tied to nitrogen. (7) In the action of reducing agents on nitrosulphonic acid an atom of hydrogen is taken up, and it is converted into nitrosisulphonic acid,



$$O=N\begin{matrix}-OH\\ -SO_2-OH.\end{matrix}$$

This acid is soluble in concentrated sulphuric acid with a fine blue colour; in weaker sulphuric acids it produces only a slight red colour which on addition of a few drops of cupric sulphate solutions changes into vivid purple. Nitrosisulphonic acid is very easily split up into NO and H_2SO_4. The estimation of nitrogen in Lunge's nitrometer is based on the formation and decomposition of this compound. [The formula given to this "nitrosisulphonic acid" involves the assumption of quadrivalent nitrogen!—G. L.] (8) Nitrosisulphonic acid forms with copper and iron salt-like compounds of somewhat greater stability. Differing from the free acid, these compounds do not split off any NO when shaken with strong sulphuric acid. Hence the nitrogen of substances containing copper and iron cannot be estimated by means of the nitrometer. (9) Nitrosisulphonic acid is also formed when SO_2 meets with nitrosulphonic acid, but only when this has been previously split up into nitrous acid and sulphuric acid. It is, therefore, not formed by a reduction of nitrosulphonic acid, but by the fact that the nitroso-sulphonic acid, $ONSO_3H$, previously formed from a molecule of nitrous acid and a molecule of sulphurous acid, is immediately transformed with a second molecule of sulphuric acid into nitric oxide and nitrosi-sulphonic acid. (10) Exactly in the same way nitrosulphonic acid in the Glover tower yields first nitrous acid, then nitroso- and nitrosi-sulphonic acid, and ultimately nitric oxide and sulphuric acid. The nitric oxide is again oxidised into nitrous acid, which again combines with sulphurous acid, and as final products again yield nitric oxide and sulphuric acid, and so forth. (11) The same circle of reactions is continued in the lead chambers. Both the chamber-process and the formation of sulphuric acid in the Glover tower are expressed by the equations:

$$1.\ \mathrm{ON.OH + SO_2 = ON.SO_2.OH.}$$

$$2.\ \mathrm{ON.SO_2.OH + ON.OH = NO + ON}\begin{matrix}\mathrm{—OH} \\ \mathrm{—SO_2.OH.}\end{matrix}$$

$$3.\ \mathrm{ON}\begin{matrix}\mathrm{—OH} \\ \mathrm{—SO_2.OH}\end{matrix} = \mathrm{NO + H_2SO_4.}$$

$$4.\ \mathrm{2NO + O + H_2O = 2ON.OH.}$$

The first of these reactions is reversible. If it has taken place, the second follows immediately. The third goes on all the more quickly, the higher the temperature; it may entirely cease during disturbances in the chamber-process, especially when the reactions 1 and 2 are continued up to the cool Gay-Lussac tower; in that case the acid flowing from that tower shows a pink colour. The fourth reaction at ordinary temperatures requires three seconds for its completion; at the higher temperature of the chambers probably even less. (12) This whole theory Raschig claims to be essentially the same as that which he pronounced in 1887 and again affirmed in 1904. Only his former second equation, which he himself in 1904 admitted to be somewhat uncertain, is now separated into two equations, Nos. 2 and 3, each of which he claims to have proved as correct.

In the *42nd Report on Alkali Works*, for 1905, p. 19, where Raschig's paper is mentioned, it is stated that in Great Britain experience has abundantly proved that it is practically impossible to avoid disorganisation of the chamber-process when working with a notable excess of SO_2 in the last chamber; it is most difficult to control the amount of such excess within the limits desired, and escapes from the exit of the process beyond those prescribed by the statute are then most liable to occur. The aim of most acid-makers of experience has been to reduce such excess of SO_2 to a minimum consistently with preserving the lead work of the back chambers from attack by nitric acid, which is a reaction product under conditions of absence of SO_2.

The preceding publication of Raschig's caused Lunge, this time in conjunction with Berl, to take up that subject again. The results of their work in that field are contained in the *Z. angew. Chem.*, 1906, pp. 807 to 819, 857 to 869, and 881 to 894. In the first instance they made an extensive experimental investigation of the behaviour of the nitrogen oxides, in order to ascertain whether Raschig's objections to Lunge's analytical methods for these oxides are well founded or not. Liquid nitrogen peroxide was prepared in a state of complete purity, and in specially constructed apparatus brought into contact, both with concentrated sulphuric acid and, on the other hand, with decinormal caustic-soda solution. Their numerous and most careful experiments were in complete accordance with Lunge's former statements; both liquid and gaseous nitrogen peroxide, diluted with air or oxygen, give absolutely correct analytical results by absorption in sulphuric acid and testing that solution for total nitrogen in the nitrometer, and for the degree of oxidation by potassium permanganate, if the amount of water present with the N_2O_4 is taken into consideration. In opposition to Raschig's contention on the slow rate of absorption of N_2O_4 in concentrated sulphuric acid, which was founded on partly objectionable experiments, they found the velocity of absorption to be immeasurably great. In making these experiments they had to construct special apparatus, in order to assure the absence of any errors. They also point out various important sources of error in Raschig's way of proceeding. Most distinctly they refute Raschig's assertion concerning the splitting off of oxygen by the action of sulphuric acid on nitrogen peroxide, which, he asserted, must lead to the formation of free nitrogen and nitrous oxide, both of them valueless, in sensible quantities; thereby also Raschig's conclusions on the technical part of the absorption of nitrous gases are shown to be worthless.

Lunge and Berl then proceed to discuss the formation of nitrogen trioxide, N_2O_3, and its existence in the gaseous state. They point out how monstrous is Raschig's attempt at brushing away the physical proofs for the splitting up of N_2O_3 into NO and NO_2 on vaporisation, and his maintaining the formation of N_2O_3 from NO and O by the bold words. "Avogadro's hypothesis is, therefore, false." That means denying one of the fundamental laws of physics and chemistry, which involves also a denial of the kinetic theory of gases and of the modern theories on dissociation, and is absolutely irreconcilable with the work of so many investigators in that field. Such a monstrous assumption is all the less excusable, as Lunge and Berl have also destroyed Raschig's arguments founded on erroneous analytical methods. We must refer the reader for details to the original paper, and we now give only the final conclusions proved by Lunge and Berl's work.

(1) Liquid nitrogen peroxide, as well as the mixture of NO_2 and N_2O_4 formed on its vaporisation, are quite accurately analysed by absorption in concentrated sulphuric acid by means of an efficient apparatus, also when they are diluted with large quantities of air or pure oxygen or pure nitrogen. The proportion of oxygen to nitrogen found in the absorbing-acid is exactly that which follows from a splitting up of nitrogen peroxide in the sulphuric acid into equal molecules of a nitroso-compound (SO_3NH) and a nitro-compound (HNO_3). Raschig's results, which are in contradiction with this, must needs be erroneous.

(2) Dilute caustic-soda solution gives equally correct results for nitrogen peroxide, when this is brought into contact with it either in the liquid state or as a vapour, diluted with an inert gas (nitrogen). This holds good both of the total absorption and of the proportion between nitrite and nitrate. If, however, gaseous nitrogen peroxide is mixed with oxygen or atmospheric air, the nitrite, in the moment of its formation, is partially oxidised into nitrate, thus increasing the quantity of the latter. Such mixtures, therefore, must *not* be analysed by absorption in dilute soda-solution, as Raschig's has attempted to do. This rapid action of free oxygen on sodium nitrite *at the moment of its formation*, while that action on *finished* sodium nitrite is very slow, constitutes a new fact of considerable importance in some technical questions.

(3) Gaseous mixtures containing, besides nitrogen peroxide, also nitric oxide, up to the molecular proportion $NO + NO_2$, on absorption in concentrated sulphuric acid also give correct results. Probably in the first instance the peroxide forms nitrososulphuric acid and nitric acid; but the latter is instantaneously reduced to nitrososulphuric acid by the NO, so that

there is no loss of nitrogen compounds, and a mixture of equal molecules of NO and NO_2 has the same action as if N_2O_3 were present. If more NO is present than in the ratio of 1 mol. NO to 1 mol. NO_2, that excess must escape unabsorbed.

(4) Mixtures of the kind mentioned in No. 3 must not be analysed by absorption in dilute caustic-soda solution, as in this case the total absorption is incomplete, and moreover the proportion between nitrite and nitrate is wrongly turned to the increase of the latter. The reason of these faults is this. At the first moment the soda solution, like the sulphuric acid, dissolves the nitrogen peroxide with formation of nitrate and nitrite, but the reducing-action of the equally present NO on the $NaNO_3$ is much too slow even at the moment of formation, and therefore much NO thus escapes absorption. Hence in this case (and doubtless in many others) a mixture of equal molecules of NO and NO_2 does *not* act like N_2O_3.

(5) The losses observed by Raschig on the absorption of nitrogen peroxide by concentrated sulphuric acid, and ascribed by him to a splitting-up into N_2O or N and ozone, and to the comparatively slow rate of solution of the nitrogen peroxide in the acid, do not take place in the case of proper manipulation. The absorption is, in fact, quantitative; the apparent loss (which could be reduced to 3 per cent.) was experimentally proved to be due to the attraction of moisture by the liquid peroxide on weighing it out. Contrary to Raschig's assertion, the velocity of absorption of the nitrogen peroxide is extremely great, not merely in sulphuric acid of full concentration, but also in 80 per cent. acid.

(6) The use of india-rubber for stoppers or joints, unless these are specially protected, in the presence of nitrous gases causes considerable errors in analyses, and any tests made with apparatus of this kind are unreliable. This does not apply to nitric oxide in such cases where no oxygen gets mixed with it (which of course produces higher oxides of nitrogen).

(7) If NO is brought into contact with an excess of air and water, there is, contrary to Raschig's assertion, a formation of nitric acid, even when the mixture is immediately shaken up, over and above the amount produced when dissolving NO_2 in water, and this is especially owing to the oxidation of the aqueous solution of nitrous acid by atmospheric oxygen. The

action of water assumed by Raschig, which is from the outset most unlikely and is called by him "most remarkable," and which, as he thought he had found, consists in dissolving from a mixture of NO_2 and N_2O_3 only the former, has no existence.

(8) The oxidation of NO leads directly to peroxide, without going through the intermediate stage of N_2O_3. The break in the reaction-curve assumed by Raschig to take place at the point when NO has passed very quickly into N_2O_3, which after that point passes, as he states, much more slowly over into N_2O_4, can be deduced neither from his experiments nor from Lunge and Berl's. On the contrary, in all cases, both when working with pure oxygen and with atmospheric air, a steady curve is found, just as must be expected from the kinetics of reaction in case of a simple time reaction: $2NO+O_2=N_2O_4$. It was unmistakably proved that this reaction does not go on instantaneously, but requires a certain time during which, besides molecules of N_2O_4, NO_2 and oxygen in excess, there is always some NO present. The reaction: $2NO+O_2=N_2O_4$ $(2NO_2)$ is a trimolecular one.

(9) The arguments given *sub* No. 8 have absolutely disproved Raschig's argumentation for the initial formation of N_2O_3 from NO and O (whether pure or mixed with N). Since, as admitted by himself, there is no other "chemical" proof possible for the existence of gaseous N_2O_3, and since all former work founded on physical observations leads to admitting the existence of gaseous N_2O_3 at ordinary temperatures only to a minimal extent, and not all above 50°, there exists no possibility of assuming the presence of gaseous N_2O_3 in the atmosphere of the lead-chamber, and of basing thereon any theories of the chamber process.

(10) By the proof that Raschig's arguments for the existence of sensible quantities of N_2O_3 in the gaseous state are unfounded, also his attack on Avogadro's law has been rebutted.

(11) Raschig's assertion that the chamber crystals, SO_5NH, are to be considered as nitrosulphonic acid, not as nitroso-sulphuric acid, cannot be submitted to any proof for the solid crystals; but for this solution in sulphuric acid in any case the "nitroso" formula must be regarded as the right one.

(12) Raschig's theory of the lead-chamber process, developed in his publications of 1888, 1904, and 1905, is untenable, firstly,

because it entirely ignores the formation of nitrososulphuric acid, which takes place everywhere and necessarily; secondly, because as an essential intermediate "link" it introduces a compound never up to this moment produced even in traces, viz.: his "nitrososulphonic acid," by which assumption not the slightest advantage is gained; thirdly, because an inevitable consequence of his theory would be the formation of *considerable* quantities of nitrogen protoxide, hydroxylamine and ammonia in the vitriol chambers, which certainly does not take place; fourthly, because his theory demands a continuous formation and action of nitrous acid which cannot be found in the atmosphere of the chambers either as such or in the form of the anhydride, nitrogen trioxide.

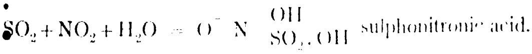
Under all circumstances the assumption of the hypothetical nitrososulphonic acid is absolutely superfluous, since sulphonitronic acid (*cf.* No. 14) is formed directly from SO_2, NO_2, and H_2O.

(13) Nitrososulphuric acid acts as oxygen carrier, which fact is most easily proved in the nitrometer, but must naturally be applied to other cases as well, and comes out in the series of reactions enumerated *sub* No. 15.

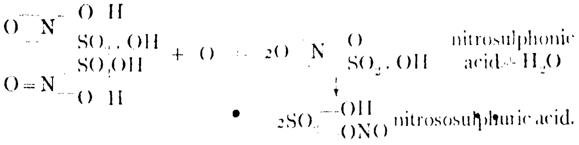
(14) The blue compound SO_5NH_2, already brought in by Trautz, which has been quoted *suprà* as "sulphonitronic acid," and which has been assumed also by Raschig in his newest paper (under the name of "nitrosisulphonic acid") to act as an intermediate link between his hypothetical nitrososulphonic acid and sulphuric acid, is actually formed, although only transiently, on the action of nitrogen peroxide or of nitrous acid on sulphurous acid, and also on the reduction of nitrososulphuric acid. It most easily passes over into the last-mentioned acid, either by the action of free oxygen or by oxidation by means of NO_2 with a splitting-off of NO. Nitrososulphuric acid, on its part, afterwards either passes over by hydrolysis into sulphuric acid and nitrous acid (which, however, cannot exist for a moment in the atmosphere of the chamber, where it is instantaneously split up into H_2O, NO, and NO_2), or else, as in the Glover tower, it reacts with SO_2, forming sulphuric acid and again sulphonitronic acid, which, as above mentioned, is oxidised by free oxygen or by NO_2. The NO formed from the latter is of course again changed into NO_2 by the atmo-

spheric oxygen. Besides this, may also occur the splitting-up of sulphonitronic acid into NO and H_2SO_4, which takes place in the nitrometer, and which in Raschig's last paper is also assumed to take place in the lead-chambers.

(15) From the points enumerated we must infer that the theory of the lead-chamber process, pronounced by Lunge in 1885, retains its validity in all essential respects, but that the equation: $2SO + NO + NO_2 + O_2 + H_2O = 2SO_5NH$, the left side of which shows too many molecules as reacting upon one another, should be replaced by simpler equations through the introduction of the *proved* formation of sulphonitronic acid as intermediate link. This modified theory is represented by the following equations:—

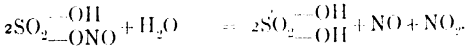
1.


$$SO_2 + NO_2 + H_2O = O{=}N\begin{smallmatrix}OH\\ SO_2.OH\end{smallmatrix} \text{ sulphonitronic acid.}$$

2ª.


$$\begin{matrix}O{=}N\begin{smallmatrix}OH\\ SO_2.OH\end{smallmatrix}\\ O{=}N\begin{smallmatrix}SO_2OH\\ OH\end{smallmatrix}\end{matrix} + O = 2O{=}N\begin{smallmatrix}O\\ SO_2.OH\end{smallmatrix} \text{ nitrosulphonic acid} + H_2O$$
$$\downarrow$$
$$2SO_2\begin{smallmatrix}-OH\\ -ONO\end{smallmatrix} \text{ nitrososulphuric acid.}$$

2ᵇ. $2SO_5NH_2 + NO_2 = 2SO_5NH + NO + H_2O.$

3ª.


$$2SO_2\begin{smallmatrix}-OH\\ -ONO\end{smallmatrix} + H_2O = 2SO_2\begin{smallmatrix}-OH\\ -OH\end{smallmatrix} + NO + NO_2.$$

3ᵇ. $2SO_5NH + SO_2 + 2H_2O = H_2SO_4 + 2SO_5NH_2.$

3ᶜ. $SO_5NH_2 = NO + H_2SO_4.$

4. $2NO + O_2 = N_2O_4.$

Reactions 1, 2ª, and 2ᵇ thus show the formation, first of sulphonitronic (nitrosulphonic) acid and then that of nitrososulphuric acid. Reactions 2ª and 2ᵇ go on simultaneously and parallel, according to whether free oxygen or NO_2 prevail in a certain place in the gaseous mixture. In the same way 3ª and 3ᵇ go on parallel, viz., 3ª there where there is an excess of water, 3ᵇ there where there is less water and more SO_2. 3ᵇ then passes on to 3ᶜ, except where the reactions 2ª and 2ᵇ have taken place; this latter case must be regarded as the prevalent one in the chambers, where O and NO_2 are everywhere present as well. Hence all the reactions enumerated *sub* No. 3 lead to the formation of sulphuric acid.

In order to facilitate understanding these reactions, we shall now give them, not in structural, but in simple formulæ:—

1. $SO_2 + NO_2 + H_2O = SO_5NH_2$
2. $2SO_5NH_2 + O = H_2O + 2SO_5NH$
3^a $2SO_5NH + H_2O = 2H_2SO_4 + NO + NO_2$
3^b $2SO_5NH + SO_2 + 2H_2O = H_2SO_4 + 2SO_5NH_2$
3^c $SO_5NH_2 = NO + H_2SO_4$
4. $2NO + O_2 = N_2O_4$.

We here interpose a short notice of a controversy between M. Neumann and the author of this treatise, the papers referring to which appeared shortly after Lunge and Berl's communication, of which we have given an abstract in the preceding pages, 1024 *et seq.* These papers are by Neumann (*Z. angew. Chem.*, 1906, pp. 1702 to 1708); Lunge (*ibid.*, pp. 1931 to 1933); Neumann (*ibid.*, 1907, pp. 264 to 267); Lunge (*ibid.*, pp. 267 to 268). In his first paper Neumann pronounces his essential agreement with Lunge's theory of the lead-chamber process in its former shape, which he assumes to have been quite materially changed in the paper by Lunge and Berl, *suprà*; Lunge's reply shows that this assumption is unfounded, and that the other objections made to various statements of Lunge's are equally groundless. In his second paper Neumann upholds his views, and Lunge finally replies in the last of the above-mentioned papers. We cannot here find space to go into particulars on this controversy, by which the subject in question has not received any material further elucidation. We only mention that Neumann has taken out a Ger. P. 169729, in which he tries to combine the "reaction-towers," proposed by Lunge (*vide suprà*, p. 657), with other towers in which the reactions of the Glover-tower are to be further extended. We must confine ourselves to this short notice, as we cannot find out whether Neumann's system has been anywhere tried on a working scale; none of the practical men we have enquired from knew anything about it.

Remarks and discussions on the modern processes here treated by Erban and by Feigensohn in *Chem. Zeit.*, 1906, No. 71, and *Oesterr. Chem. Zeit.*, 1906, pp. 238 and 277, afford no new information on this subject.

A long paper by Littmann (*Z. angew. Chem.*, 1906, pp.

1177 to 1188) describes numerous observations he had made with lead-chambers during actual work, which (as he himself admits) offer very little novelty to those conversant with this subject. In this place we need only mention that he finds all over a formation of nitrososulphuric acid; but he considers that formation, if taking place at an excessive rate, to be rather injurious to the chamber-process than otherwise, apart from damage done to the lead. He lays great stress on dividing the gases equally, so that the atmosphere of the chamber becomes all over charged with nitrous gases, and on introducing the gases from the top. The part played by the acid lying at the chamber-bottom is also important, as it denitrates the descending nitrososulphuric acid and reintroduces the nitrous gases into the atmosphere of the chamber.

Le Blanc (*Z. Elektrochem.*, 1906, pp. 541 *et seq.*) found that caustic-soda solution frequently yields faulty results in the analysis of nitrous gases, more nitrate being found in the proportion to the nitrite than is actually present. He prefers absorbing the gases, with due agitation, in strong sulphuric acid and analysing by Lunge's methods. Most distinctly he found that N_2O_3 is formed only in minute quantities and temporarily.

Nernst (*ibid.*, p. 544) confirms that alkaline solutions do not instantaneously absorb NO_2. Le Blanc shows that on mixing NO and NO_2, an equilibrium: $NO+NO \rightleftarrows N_2O_3$ takes place, which at ordinary and higher temperatures is so far shifted to the left side of that formula, that no sensible quantities of N_2O_3 can be found by estimating the vapour pressure. Only at much lower temperatures, considerably below the liquefying point of nitrogen peroxide, N_2O_3 is stable. The above equilibrium $NO+NO_2 \rightleftarrows N_2O_3$, although containing extremely little N_2O_3, chemically behaves like N_2O_3 [which is precisely the contention of Lunge throughout the whole of these controversies].

The controversy between Raschig on one side and Lunge and Berl on the other was continued by Raschig in a long paper, *Z. angew. Chem.*, 1907, pp. 694 to 722. From his experiments he infers the existence of various hitherto unknown nitrogen oxides: iso-nitrogen-tetroxide (oxy-nitrogen-trioxide), iso-nitrogen-pentoxide, nitrogen hexoxyde (trioxynitrogen trioxide), nitrogen heptoxyde, nitrogen-iso-dioxide, about which we must refer to the original, since no other chemist up to this time has observed these substances, and the part they would play in the chamber-process, if they really existed, is quite uncertain. Raschig again upholds his denial of the truth of the law of Avogadro. He further discusses the question of the formation of nitrosulphonic acid (=nitrososulphuric acid), which he maintains to be impossible in the chambers, so that that compound cannot play the action of catalyser in the chamber-process. On the contrary he believes it to be injurious in that process, in accordance with Littmann (*supra*, p. 1031), and he again maintains his theory of the action of nitrous acid as *the* catalyser in the chamber process. He also tries to meet some special objections made to his statements by Lunge and Berl.

Caused by Raschig's just-quoted publication, Lunge and Berl (*Z. angew. Chem.*, 1907, p. 794; pp. 1713 to 1722) repeated, with the greatest possible care and every imaginable precaution against errors, their work in that field, more especially on the analytical methods for estimating the various oxides of nitrogen. Raschig had so far agreed with them that for the analysis of compounds, having the empirical composition of N_2O_3 (whether this be present as such, or as a mixture of equal molecules of NO and NO_2) in the presence of oxygen, concentrated sulphuric acid is the proper absorbent, whereas caustic-soda solution gives erroneous results; but for the estimation of nitrogen peroxide in the presence of oxygen, Raschig holds to soda solution as the only proper absorbent, because, as he maintains, with sulphuric acid the absorption is not complete and there are losses by the splitting-off of N_2O, N_2, and ozone, and other sources of error. In order to decide that question, Lunge and Berl carried out a number of experiments with the utmost care, and by means of specially constructed apparatus. To begin with, they prepared absolutely pure and dry nitrogen peroxide and submitted this to the various analytical processes, with the result that their former results were entirely corroborated, and Raschig's contentions were proved to be wrong. Another series of most carefully conducted experiments proved beyond contradiction that the action of oxygen on NO leads directly to the formation of nitrogen peroxide, the curve taking a completely continuous course, decisively excluding the assumption of any intermediary formation of nitrogen trioxide. Lastly, they repeated their experimental investigation of the reactions in the lead-chambers, and they found, when working with perfected apparatus and the utmost possible care, that the equations by which they had represented the chamber-process in their last paper (*suprà*, p. 1029) were not merely confirmed as taking place, but it was moreover proved that they go on almost quantitatively; thus once more proving that the formation of nitrososulphuric acid and its decomposition, with the intermediate stage of sulphonitronic acid, play the principal part in the chamber reactions.

To this paper Raschig made a short reply (*ibid.*, p. 1809), in which he asserts that Lunge and Berl had not entered upon his principal contentions, and he entirely maintained all his assertions concerning the processes going on in the lead-chambers.

A final reply to Raschig was made by Lunge and Berl (*ibid.*, pp. 2074 *et seq.*). They refute Raschig's accusations as to their having neglected to enter upon many of his contentions, and prove that his accusations are in every single case entirely unfounded. In their opinion nothing more can be attained by mere quarrels, and a continuation of the discussion is useless before fresh work in that field has been done, preferably by an impartial third party.

Raschig has not made any reply to the above during th years elapsed since that controversy, and we have now th right to say that the question of the reactions in the chamber stands there where Lunge and Berl left it; especially a Raschig, when opposing the theories of Wentzki and of Jurisch in 1910 (*vide infrà*) does not use that opportunity of combatin Lunge and Berl's views as just stated, and that, as we shal see *infrà*, in his lecture in 1911 he distinctly admits that th action of oxygen on nitric oxide does not produce N_2O_3, but nitrogen peroxide.

H. B. and M. Baker (*J. Chem. Soc.*, 1907; *Transactions*, ii p. 1862) assert that nitrogen trioxide can be obtained in th gaseous state, if every trace of moisture is excluded by specia precautions [a precaution, of course, the reverse of which hold good in acid-chambers].

Mandl and Russ (*Z. angew. Chem.*, 1908, pp. 486 to 491) fin that the combination of NO with oxygen leads to varyin results, according to the origin of the oxygen employed, an does not always lead to pure NO_2. They admit that their experiments are not sufficient for a final solution of the question; perhaps catalysers come into play here.

In opposition to their work, Holwech (*ibid.*, pp. 2131 to 2134), working under the direction of Professor Haber, shows that a mixture of 2 vol. NO and 1 vol. oxygen of various origin at atmospheric pressure is practically completely changed into NO_2 and N_2O_4, and that the velocity of the reaction is approximately the same, for oxygen prepared by Linde's process, or such containing ozone, or prepared from barium peroxide, potassium bichromate, and dilute sulphuric acid.

Foerster and Koch (*ibid.*, pp. 2161 to 2172 and 2209 to 2219) studied in great detail the action of a mixture of nitrogen dioxide and oxygen upon water; also the action of water on nitrogen dioxide strongly diluted with atmospheric air, and of ozone on NO_2. Their work is of very great importance concerning the formation of nitric acid (*v. suprà*, p. 184), but does not apply to the vitriol-chamber process.

Bodenstein (*Z. Elektrochem.*, 1910, p. 876) discusses the velocity of the combination of NO with oxygen, on which he has (with Meinecke) made experiments at very low concentrations, by which that reaction becomes measurable. Their results are not yet entirely concordant, and further work must be done in that quarter. Most surprising is their observation that that reaction goes on more slowly at 15° than at 0°.

Jurisch (*Chem. Ind.*, 1910, pp. 137 to 142) puts himself in opposition against both Lunge and Raschig, and all others who assume that the oxidation of SO_2 into H_2SO_4 takes place indirectly with formation of intermediate compounds. He maintains that the normal process in the chambers is represented by the equations:—

$$SO_2 + N_2O_3 + H_2O = H_2SO_4 + 2NO$$
$$SO_2 + 2HNO_2 = H_2SO_4 + 2NO$$
$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2,$$

and that all the reactions observed by Lunge and Raschig take place under abnormal conditions.

Wentzki (*Z. angew. Chem.*, 1910, pp. 1707 to 1714) also declares the assumption of intermediate stages in the oxidation of SO_2 by the nitrous gases in the lead-chambers as unnecessary, such oxidation taking place in a direct manner by nitric peroxide:

$$
\begin{aligned}
&(a)\ SO_2 + NO_2 + H_2O = H_2SO_4 + NO \\
&(b)\ NO + O = NO_2.
\end{aligned}
$$

Nitrous trioxide, he holds, is not in question, as its existence in the gaseous state (under chamber conditions) has been distinctly disproved. Lead-chamber crystals are only formed in the chambers in such places where there is a local deficiency of water, not primarily by the condensation of SO_2, NO, O, and H_2O. He objects to the constitution formula given to sulphonitronic acid by Raschig and by Lunge and Berl, and he believes that that acid cannot be formed under chamber conditions. The nitrosisulphonic acid (sulphonitronic acid) is formed in the chambers only by the action of SO_2 on an excess of nitrososulphuric acid, *e.g.* by a faulty process in the Gay-Lussac tower, and its formation is without any importance for the manufacture of sulphuric acid, or even damaging to it.

Raschig (*Z. angew. Chem.*, 1910, pp. 2241 to 2250) points out that both Jurisch and Wentzki go back to the original theory of Clément and Desormes pronounced in 1806. Jurisch has made no experiments whatever to support his views, and need not be answered. Wentzki adduces some new experiments, but he has misunderstood their bearing. Both of them overlook the fact that already in 1812 Davy had refuted the view of Clément and Desormes by pointing out that their theory inevitably leads to the assumption that SO_2 and NO_2 act upon each other also in the absence of water, forming anhydrous SO_3 and NO, which is notoriously *not* the case, a fact again proved by numerous experiments made by Raschig. This chemist also quotes a remarkable observation, communicated to him by Sauerschnig as made in the practical working of acid chambers, viz., that the chamber process is not (as might be supposed on the strength of the law of the action of masses, and would be absolutely demanded by the theories of Jurisch and of Wentzki) rendered quicker and more complete the more oxygen is present, but that the production of sulphuric acid in the chambers increases with the increase of oxygen only up to a certain optimum of the oxygen percentage, and decreases again when this optimum is exceeded. This fact is absolutely irreconcilable with the theory of a direct oxidation of SO_2, brought about by the nitrous gases as catalysers; it imperatively demands the action of intermediate products, as assumed both by Raschig and by Lunge. Wentzki has committed quite a mass of errors, both in his observations and in his argumentation on Raschig's former work, which the latter discusses in great detail, with the final verdict that his (Raschig's) theory has victoriously come out in the struggle. Raschig further disproves the contention of Manchot (*Z. angew. Chem.*, 1910, p. 2112), according to which the "blue acid" is not nitrosisulphonic acid, but is produced by traces of iron in his materials.

Berl (*Z. angew. Chem.*, 1910, pp. 2250 to 2253) also opposes Wentzki's statements and opinions, especially his denial of the formation of nitrosisulphonic acid in the chambers and that of nitrososulphuric acid. Concerning Wentzki's denial of the action of intermediate products, and his assertion of the immediate reaction: $SO_2+NO_2=SO_3+NO$, Berl points out that not merely the left side of this equation is wrong, since notoriously dry SO_2 and dry NO_2 do *not* act upon each other, but also the right side, for already in 1839 Rose, and in 1856 Brüning, observed that SO_3 and NO act upon each other with formation of dinitroso-pyrosulphuric acid, $2SO_3$, N_2O_3, and Berl, together with Jurrissen, confirmed this and prepared that acid in a pure state. Berl also points out that the chamber crystals, SO_5NH, according to the various ways of their formation and their reactions, can be formulated both as nitrosylsulphuric acid and as nitrosulphonic acid, and this is probably a case either of isomeria or of tautomeria.

Wentzki (*ibid.*, 1911, pp. 392 to 400) defends himself against Raschig and Berl. He denies the formula given by Raschig to the "blue acid," and the part attributed to it as intermediate link in the lead-chamber process; the proofs given for this by Raschig and by Berl are attributed to him to other reactions than those taking place in the chambers. He equally denies the formation of Raschig's "nitrososulphonic acid" by Raschig's method or in the chambers, and upholds the view of the direct oxidation of SO_2 by the higher nitrogen oxides. Later on (*ibid.*, 1911, p. 1468) he defends himself against the imputation of an error, made against him in the paper of Divers, to which we now pass.

Divers (*J. Soc. Chem. Ind.*, 1911, pp. 594 to 603) considers that Raschig's nitroso- and nitrosisulphonic acid do not exist, and that especially the latter is chemically impossible. The intermediate substance must have the formula $H_2N_2SO_6$, because it is the sum both of $2HNO_2 + SO_2$ and of $2NO + H_2SO_4$, that is, of the active substances and of the final products. This intermediate substance he calls nitroxysulphuric acid; it is sulphonated nitroxous acid, this being the name given by Divers to Thurn's azohydroxyl or Angeli's nitrohydroxamic acid, $H_2N_2O_3$, an acid half-way between hyponitrous and nitrous acids. His constitutional formulæ are: nitroxous acid, $HON\overset{O}{\underset{O}{}}NH$; nitroxysulphurous acid, $HON\overset{O}{\underset{O}{}}NSO_2H$; nitroxysulphuric acid, $HN\overset{O}{\underset{O}{}}NSO_3H$. An explanation can now be given of the long-recognised peculiarity that the volume of atmospheric oxygen which must enter the lead-chamber is, roughly measured, equal to that of the SO_2 and, therefore, twice as much as has seemed chemically necessary. That explanation rests upon Raschig's observation of the atmospheric oxidation of nitric oxide. The immediate product has the composition N_2O_4, but for a short time differs from ordinary nitric peroxide in being nitrous peroxide, ONO – ONO, which acts upon water as a nitrous compound, oxygen being liberated. Since SO_2 needs as much nitrous acid as that derived from 2NO, and 2NO combines with O_2 as nitrous peroxide, the process in the lead-chamber is expressed by the equations:—

$$2NO + O_2 = ONO - ONO$$
$$2N_2O_4 + 2H_2O = 4HNO_2 + O_2$$
$$2HNO_2 + SO_2 = H_2N_2SO_6 = 2NO + H_2SO_4.$$

These equations show all the oxygen as used up, temporarily by the nitric oxide, yet only to produce the peroxide of nitrous acid ONO – ONO. Since, outside the chamber, nitrous acid so steadily unites with two molecules of SO_2, it has been hitherto a difficulty to understand how in the chambers, where SO_2 is present in large excess, nitrous acid should there combine with so much less SO_2. Divers thinks the reason of this to be that the nitroxysulphuric acid, as fast as it is formed, produces the chamber mist, consisting of minute drops of sulphuric acid, surrounded each by an atmosphere of unmixed nitric oxide. The NO, diffusing into the chamber atmosphere of SO_2 and O_2, largely diluted with nitrogen, is in excess of the SO_2 and O_2 which it meets, until it has all become nitroxysulphuric acid, which is itself unacted upon by the constituents of that atmosphere.

In a lecture given in London in 1911 (*J. Soc. Chem. Ind.*, 1911, pp. 166 to 172), Raschig upholds his former views (without entering in any way on his polemics with Lunge and Berl), and he gives the following equations for the reactions going on in the chambers:—

(1) $2NO + H_2O + O = 2HNO_2$
(2) $HNO_2 + SO_2 = ONSO_3H$
(3) $HNO_2 + ONSO_3H = NO + H_2NSO_5$
(4) $H_2NSO_5 = NO + H_2SO_4$,
in summa: $SO_2 + O + H_2O = H_2SO_4$.

He *now* admits the non-formation of gaseous N_2O_3, and records his conviction that the product of the oxidation of nitric oxide is nitrogen peroxide: $NO + O = NO_2$.

Reynolds and Taylor (*J. Soc. Chem. Ind.*, 1912, pp. 365 *et seq.*) show that Raschig's explanation of the vitriol-chamber process by the interaction of nitrous and sulphurous acid with formation of the hypothetical intermediate products: nitrososulphonic and nitrosisulphonic acid, is founded on experimental errors. According to them the only gaseous product of the action of SO_2 on nitrous acid is nitrogen protoxide. The nitric oxide, found by Raschig in his experiments, had been formed by the presence of potassium iodide, used as an indicator. Chamber-crystals can exist in solution in sulphuric acid of 60 per cent., which fact refutes Raschig's explanation of Sabatier's purple acid (Raschig's nitrosisulphonic acid). These facts are equally incompatible with the modifications of Raschig's theory proposed by Divers (*suprà*).

CHAPTER VI

THE RECOVERY OF THE NITROGEN COMPOUNDS

THE recovery of the nitrogen oxides which are still present in the gaseous mixture issuing from the last chamber has been previously mentioned as a process indispensable for the rational manufacture of sulphuric acid. It saves not merely at least two-thirds of the nitre, but also a great deal (a quarter up to a third) of the chamber-space; it increases the yield of sulphuric acid, and, moreover, prevents the escape of acid fumes into the atmosphere. Several processes may be employed for this object; but, with one exception, they only require to be briefly mentioned. The only plan which has turned out successful in manufacturing practice, and which, certainly after a considerable length of time, has been introduced into all well-managed works, is that which was proposed by Gay-Lussac as early as 1827, viz., the *absorption of the nitrous fumes by strong sulphuric acid.* The chemical fact underlying this process, viz., the behaviour of the oxides and acids of sulphur and nitrogen towards one another, has been fully discussed in Chapter III. (pp. 330 *et seq.*), to which we must refer. We shall here examine the technical means employed for realising the possibility of recovering by far the greater part of the nitre contained in the exit-gases from the vitriol-chambers. We recall, therefore, only the following reactions.

Moderately concentrated sulphuric acid absorbs from gaseous mixtures no *nitric oxide* except in the presence of oxygen, when of course higher nitrogen oxides are formed. *Nitrous acid* is absorbed with the formation of nitrososulphuric acid:

$$2H_2SO_4 + N_2O_3 = 2SO_2(OH)(ONO) + H_2O.$$

Nitrogen peroxide is absorbed with formation both of the just-named compound and of nitric acid:

$$H_2SO_4 + N_2O_4 = SO_2(OH)\ (ONO) + HNO_3.$$

Nitrososulphuric acid is *decomposed* by water alone:

$$2SO_2(OH)\ (ONO) + H_2O = 2H_2SO_4 + N_2O_3,$$

or by water and SO_2:

$$2SO_5NH + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The most frequently used *apparatus for retaining the nitrous fumes* by means of strong sulphuric acid is the *coke-tower*, first proposed in 1827 by Gay-Lussac (who was acting as consulting-chemist to the St Gobain Co. at Chauny), and justly designated everywhere by the name of its inventor. From the facility which this apparatus gives of retaining at least two-thirds of all the nitre, and from the other important advantages realised by it, it might have been expected that it would have been generally introduced within a short period after its invention. But, most curiously, Gay-Lussac's invention was only carried out into practice for the first time in 1842, at Chauny; and forty years after its invention the majority of sulphuric-acid makers did not possess either Gay-Lussac's or any other apparatus for retaining the nitrous fumes; nay, even some of those who had adopted it in the first instance had abandoned it again.

The cause of this was that formerly the only practicable plan of recovering the nitre from the nitrous vitriol obtained in the Gay-Lussac tower consisted in diluting it with water, and that the expense of reconcentrating and of pumping the acid, etc., was thought to amount to nearly as much as the saving of nitre. Most manufacturers were not aware that the saving (which was mostly estimated too low, viz., equal to one-half of the nitre) was not the only advantage of the absorbing-towers. But the great dearth of nitrate of soda which occurred about the years 1868-1870 brought the matter vividly before them; at the same time on the Continent the composition of the chamber-gases, the chamber-space, etc., were studied more closely, and the advantage of an excess of nitrous gas in the chambers, which can only be secured by means of an absorbing-tower, became evident. These circumstances led to the erection of many Gay-Lussac towers, and the more so as some manufacturers had never given them up at all and had done very well with them.

In England, where the theoretical part of the subject has been much less attended to, another practical invention had in the meantime been made, which entirely removed the only essential drawback of the Gay-Lussac absorbing-tower, viz., the necessity of reconcentrating the acid after denitrating it by dilution; this was the *Glover tower.* Whilst about 1870 only a comparatively very small number of English works absorbed their nitre-gas at all, since then all the larger and better works have introduced the Gay-Lussac absorbing-tower, nearly always together with Glover's denitrating-tower. Probably some few exceptions may still survive; but we are here only speaking of somewhat rationally managed factories.

Gay-Lussac's Absorbing-Tower for Nitrous Gases

consists of a chamber, placed at the end of the set of lead chambers, much higher than wide (a "tower" or "column"), of which the walls are made of a material capable of resisting sulphuric acid, and the interior space is filled with a material presenting a large surface. By means of this "packing" a stream of sulphuric acid entering the column from above is divided into small drops; at the same time the current of gas rising up in the tower is divided into many small jets; and thus the contact between the gas and the acid, covering the surface of the packing, is multiplied. The principle applied here is exactly the same as had been already employed for a long time in the "scrubbers" of gas-works, in order to deprive the gas of ammoniacal salts by washing it with water, and which is also applied to the condensation of hydrochloric acid in the decomposition of common salt: it is always this, to produce a great many points of contact between the gas and the absorbing agent, and thereby to wash out the absorbable substance of the gas as much as possible; or the interior of the tower may be represented as a filter which allows only the inert gas to pass, but retains the gas acted upon by the absorbing agent.

The reason why such an apparatus is constructed in the shape of a tower or column (that is why it is made much higher than wide) is this, that in the case of apparatus with a considerable horizontal section it is very difficult to distribute a comparatively thin stream of the absorbing liquid equally over the whole section, and at the same time to force the gas to meet the liquid all over. Of course, the gas has always a tendency to rise where its progress is not barred wholly or in part by a liquid; unless the absorbing-vessels are pretty narrow, it is not possible to prevent the liquid running down almost entirely in some places, the gas rising in others, so that but little of the two would come into contact, and the liquid would arrive at the bottom charged with very little absorbable matter, whilst the gas issuing at the top would still contain a good deal of it.

From this follows this general principle:—An apparatus for the absorption of gases, such as those under consideration, should be made no wider than is necessary in order that the draught may not be impeded by the packing; and the necessary cubical volume of the packing should be obtained by making the tower so much higher. Thereby another object is also attained—viz., the gas entering at the bottom of the tower, where it is richly charged with absorbable matter, meets a liquid containing already a good deal of the same, and therefore not capable of dissolving much more, unless an abundant supply is presented to it, which is just the case under these circumstances; on the other hand, the gas near the top of the tower, where it is almost entirely deprived of its absorbable parts, meets entirely fresh liquid, which is able to seize upon those parts even in a poor gas, whilst a partly saturated liquid would have no action upon such a gas. This is the theoretical explanation of the practical fact that a *saturated* absorbing liquid, together with *exhaustion* of the gas, can only be attained by building the towers very high.

A considerable vertical height of the absorbing medium can be also obtained by placing two towers alongside each other, and compelling the gas leaving the first tower at the top to pass downwards in order to rise again in the second tower. As a rule this arrangement is not to be recommended, for two reasons:—First, there is a loss of draught caused by compelling the gas to travel downwards for a portion of its course, and the consequent great friction in the connecting-tube; secondly, in this way certainly the gas can be completely washed out, but at the same time we do not obtain a saturated absorbing-liquid, both of the towers having to be fed with liquid, which at the end only attains *half* the degree of saturation that would have been attained in *one* tower equal in height to both those employed and fed with a single jet. Where the strength of the absorbing-liquid is of no consequence, it is often more convenient to employ two towers in series than one of double the height. With the large Gay-Lussac space employed by many works it is certainly found impossible to do with only one tower. In that case two towers are employed, the first being fed with the acid run down in the second after pumping it up again. An arrangement decidedly to be rejected is found in many books and in a few badly arranged works, where, from mistaken economy, the absorbing-tower is made of twice the usual horizontal section, and divided into two halves by a partition, in order to pass the gas up one half and down the other. The saving in cost as against two towers or a tower of double the height is not very considerable; on the other hand, that half of the tower in which the gas has to descend is almost entirely sacrificed, because here, where the gas and the liquid travel in the same direction, their mutual action, as experience shows, is very inconsiderable; both mostly travel downwards peacefully without interference and arrive at the bottom almost unchanged. The arrangement of a double tower is inadmissible unless the partition extends right through, and the gas issuing from the one division passes downwards by a special pipe, and is allowed to ascend again in the second division, and thus to *meet* the acid rain. This answers the same purpose as placing two towers alongside each other.

As far as the *width* of the Gay-Lussac tower is concerned, it should be considerably wider than an empty tube of sufficient diameter for the current of gas, not merely because the packing of the tower occupies a large portion of its section and only leaves a small portion of it as clear space, but also because the packing must be purposely arranged so as to divide the current of gas into a great many separate jets, constantly changing their direction, and to expose them to the largest possible amount of *contact* with the surfaces of the packing wetted with the absorbing-liquid. The tower must therefore be wide enough to take account of this purposely increased friction.

Furthermore, it has to be considered that the *slower* the current of gas, the more time will be afforded for the action of the absorbing-liquid, and the more perfect that action will be. This would point to giving the tower as wide a section as possible, in order to slacken the speed of the gaseous current. As, for the reasons stated above, this plan has various drawbacks, the inference is that a certain middle path should be taken: the tower should be made wide enough not to hinder the draught, and to leave sufficient time for the contact of the gas and the liquid, but not so wide that the liquid cannot be spread equally all over and that the gas can go past it. Evidently no exact calculations can be made as to the proper width; experience only can decide this point. Formerly it was assumed that ordinary coke-packed Gay-Lussac towers ought not to exceed 7 ft. in width in order to secure a uniform distribution of the gas and the acids, but later on towers up to 14 ft. have been erected and no drawbacks are reported to have been caused by this extreme width.

The dimensions of the Gay-Lussac tower necessarily correspond to those of the set of chambers to which it belongs; its cubical contents should be *at least* 1 per cent. of the chamber-space. For sets of from 140,000 to 200,000 cub. ft. the column might be 6 ft. in width and 50 ft. high; for a set of from 70,000 to 100,000 cub. ft. a tower from 4 to 5 ft. in width and 40 ft. high is sufficient. In both cases it is best to give the tower an additional height of 10 ft.; there will be all the more saving of absorbing acid the higher the tower and the longer the acid has to travel. These statements refer to chambers working with pyrites; with brimstone the height of the tower need not exceed 26 ft.

Undoubtedly a larger absorbing-space, say 2 per cent. of the chamber-space, permits working with a larger economy of nitre than the above-stated sizes; in the case of large sets this space will mostly have to be divided into two towers. In fact, when the absorbing space at the Jarrow chemical works was raised to 90 cub. ft. per ton of pyrites per week, which amounts to about 2 per cent. of the chamber-space, the consumption of nitre was brought down from 1·45 to 1·05 part per 100 parts of pyrites. Similar results have been obtained elsewhere, for instance at Runcorn.

At the Oker works, one set has three Gay-Lussacs working parallel, each 3 ft. 9 in. wide and 32 ft. high, capacity 1300 cub. ft. = 1·09 per cent. of the cube of the chambers. The other four sets have similar towers, of cubic capacities = 1·30, 1·45, 1·70, 0·96 of the cube of the chambers. They are packed with coke, and are fed with acid of 60° B. = 142° Tw., 100 to 130 per cent. of the daily production. In one case a small plate-tower is also employed as preliminary Gay-Lussac tower, with excellent results (cf. *infrà*).

At the different works belonging to the Saint-Gobain Chemical Company (the largest in France) the real working-space (*i.e.* that occupied by the coke packing) of the Gay-Lussac towers formerly amounted to rather more than 5 cb.m. (say 180 cub. ft.) per ton of pyrites burnt in twenty-four hours, or from 0·7 to 1 per cent. of the chamber-space. But recently this has been very much enlarged, and now amounts to 13 or 15 cb.m. (say 455 to 525 cub. ft.) per ton of pyrites, or from 2 to 3 per cent. of the chamber-space, with a special view to "forced work" (pp. 639 *et seq.*). This does not comprise the space below the grates, that above the packing, and that occupied by the brick lining, whilst in most other statements the whole space within the leaden shell is included.

The *foundations* of the tower must, of course, be very substantial, and, if possible, constructed in such a way that any acid running over will not damage them. It is preferable to place the towers high enough to avoid the gas from the last chamber having to descend towards the tower; if, however, the chambers are very high above the ground, this would involve considerable difficulty and expense, and the tower is then raised only high enough above the ground to leave a natural fall from its bottom to an acid-tank, and from this to the pumping-apparatus for the nitrous vitriol.

The foundations usually consist of a solid block of brickwork or stones, or else of two strong pillars surmounted by an 18-in. arch. Sometimes cast-iron columns are employed, on which are placed iron girders, and crossways on these iron T-shaped bearers (usually railway-rails), close together so as to form a continuous platform. These (as well as any brick- or stonework) must be well painted with (frequently renewed) tar-paint, and must be covered at the top by a leaden apron, which directs all the drips past the pillars into a safe place, where the foundations or pillars cannot be touched by it. (The same plan should be followed for the foundations of Glover towers.)

The *framework* of Gay-Lussac towers is sometimes made of angle-iron, but more frequently of timber. In the case of towers of an angular section such frames are constructed in the usual way, as is seen in our diagrams of Gay-Lussac towers. Circular towers of moderate section are best made with a frame of four uprights, placed in the corners of a square; to these, at every 6 ft. of height, metal brackets are fixed; from these are suspended, by means of hooks, broad iron hoops (say 3 in. wide), which closely gird the tower and support its lead shell. Wide towers are built like circular Glover towers (see these).

The timber frame must be kept clear of the lead, just as in the case of the vitriol-chambers (p. 603); this, of course, is even more necessary in the case of the Glover tower (see below).

In most cases the Gay-Lussac tower is made of *lead.* The lead in continental works is sometimes unnecessarily thick, from 14 to 28 lb. to the square foot; in British works it is often no more than 7 lb. or even 6 lb. to the square foot, like the chamber-lead. It is, however, better to make the tower of 8 lb. lead, the bottom being a pound or two stronger. There is no reason why the lead should be stronger than this: the gas as well as the acid in this apparatus are only moderately warm, and, indeed, should be as cool as possible; nor is the lateral pressure of the coke, if properly packed, so great that it need cause any fear. At all events the lead sides are necessarily supported by a frame. Both *circular* and *square* towers are employed; the former take less lead for the same area. They are frequently lined inside with bricks, which are put in dry along with the packing; "split bricks" of 1-in. thickness are often employed for this purpose, lest too much space should be lost. The object of this lining is to prevent the coke from cutting the lead in settling down. It seems, however, hardly worth while to go to the expense of the lining, and at the same time to lessen the area of the tower, for such a small matter, which can be easily remedied by putting on a patch of lead; the lateral pressure of the coke can only be avoided by making the lining at least 9 in. thick, which is rarely done, as it wastes too much space.

In the case of square towers, the sheets forming the sides should be in one piece from top to bottom. They are best put up by placing the roll of lead on the level of the tower-bottom, unrolling it, supporting the remainder of the roll as it rises upwards and putting the straps in their places as the roll goes up. This is a much safer plan than the other: hoisting the whole roll of lead to the top and allowing it to unroll, gradually fixing the straps all along.

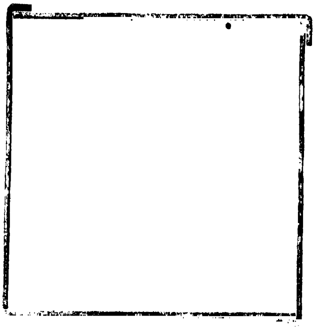


Fig. 266.

The sheets forming the sides should be turned over at the corners in order to make a joint with the next sheet (Fig. 266). The overlaps of the seams must, in every case, be placed outside (also in the case of the Glover tower); otherwise they would be quickly destroyed. The bottom is made of a single sheet, the four edges being turned up to form the upstand. The corners are not cut out and burnt, but are simply folded up as shown in Fig. 267.

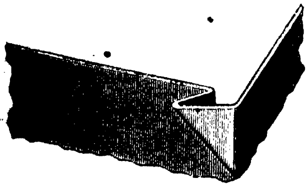


Fig. 267.

Circular towers are built up of annular drums, one above the other, each being supported by straps nailed to the upright posts, or, preferably, fixed in such a way that the overlap of the seam is turned over 3-in. iron hoops suspended from the uprights (p. 788). This plan at the same time protects the hoops and gives an excellent stay to the tower. If there are more than four upright posts, one or more of them must be left out during the building of the tower, to get the leaden drums in.

In the south of France octagonal Gay-Lussac towers are in use, built of Volvic lava (see later on), like a hydrochloric-acid condenser, without any lead shell.

All Gay-Lussac towers have an *internal filling* ("*packing*"), which at one time mostly consisted of *coke*. This material was formerly regarded as the best for this purpose, because its irregular shape and rough surfaces offer to the gas a very large area of contact with the liquid. Another advantage which coke has over other materials, as pieces of glass, earthenware, flints, etc., is its comparatively light weight. But two other advantages sometimes claimed for it, viz., porosity and resistance to chemical action, are non-existent. The contention that coke, owing to its porosity, offers a great many internal surfaces for the contact between the gas and the liquid is erroneous. In the first place, porous coke is worthless for a coke-tower, for which dense coke is indispensable; secondly, the pores must at once be filled with liquid, which thus cannot come into contact with the gas passing outside. It is not owing to its porosity, but to its rougher, more irregular, and therefor much larger *surface*, that coke is preferable to broken glass or earthenware, etc.

It is necessary to be very careful in the selection of the coke. Gas-coke is of no use at all here; only the hardest-burnt oven-coke must be used, giving a clear ring and as little porous as possible, of a silvery white, not of a dull black. It must be carefully packed, rejecting all dull black pieces. First only the large pieces, a foot and upwards in length, are picked out; these are placed in horizontal layers directly over the grating of the tower, crossing each other if possible; each piece must be placed by hand, inconvenient as it is that the workman has to be lowered from the top to the bottom of the tower, and must receive his material in the same manner. Thus the first third of the tower is packed; then come the pieces next in size; and for the last third the smaller lumps may be used, and may be simply emptied in out of baskets. Nothing, however, is allowed to go into the tower which has not been sifted through a riddle with 3-in. holes. Unless a coke-tower is packed most carefully, either the draught through it will be impeded, or there will be too much way left for the gas, or, in the most frequent and worst case, the packing will be too loose in some places and too dense in others; and thus there will be bad absorption as well as bad draught.

Soft porous coke must be rejected for two reasons; first, it cannot support the pressure of the superjacent column without being crushed, thus stopping the draught; secondly, such soft coke is soon acted upon by nitrous vitriol, and is eventually converted into a thick paste; this is very bad for the draught, and may necessitate repacking the tower. It also imparts a dark brown, at first nearly black, colour to the acid run through the tower for a considerable time (several months) after a tower has been freshly packed.

The claim formerly made for coke, that it is not acted upon by the gases or liquids within the Gay-Lussac tower, must be declared untenable even for the hardest-burnt coke, since I have shown (*J. Soc. Chem. Ind.*, 1885, p. 31) that the reason why "nitrous vitriol" never, except under totally abnormal circumstances, contains any nitric acid, even when the gases entering into the tower had contained N_2O_4, is this, that the coke reduces the nitric acid originally formed from the N_2O_4 to nitrososulphuric acid; this takes place slowly at ordinary temperatures, but very quickly and completely at slightly higher ones (30° to 40° C.), such as they generally rule in the tower.

In a subsequent investigation (*Z. angew. Chem.*, 1890, p. 195) I showed that the action goes further, and that nitrous (*i.e.* in this case nitrososulphuric) acid is reduced by the action of coke to nitric oxide, with formation of carbon dioxide. It is true that at the ordinary, or at a slightly raised, temperature this action is only very slow; but even then it is quite perceptible, and at temperatures above 70° it becomes very strong (*cf.* p. 350). This no doubt accounts for some of the losses in the manufacture of sulphuric acid, and it would seem to speak in favour of employing a description of packing which is not acted upon by the nitre in any way. In fact, at some works the ordinary coke-towers must be repacked every year, and in places where the coke-packing has been replaced by cylinders of hard stoneware, the nitrous vitriol is very much stronger than with coke-packing under similar circumstances.

Hallwell (*Chem. Zeit.*, 1893, p. 263) noticed a distinct saving of nitre when he replaced the coke-packing by stoneware.

Of course, dense coke is less acted upon than porous coke (as distinctly proved once more in my experiments); the latter does not even resist the action of pure concentrated sulphuric acid without disintegration. But in the end all coke is gradually wasted, and long before this is done to such an extent that the real loss of weight would make it necessary to replenish the tower, the mud formed by the disintegration of part of the coke stops up the draught to an intolerable extent. Flushing the tower with water is sometimes a remedy, but is far from being always efficacious.

In the case of very high towers, sometimes one or two grids are interposed at various heights for supporting the upper layers of the coke. These grids are made of iron bars cased in lead. Unless they are very carefully arranged, as will be shown in our drawings, they may go down with the coke packing, as the latter gradually sinks down, and may do more harm than good.

The drawbacks notoriously existing in the case of coke-packed Gay-Lussac towers have long since led to the employment of other styles of packing; as such short *cylinders of acid-proof stoneware* are mostly used, of which we shall speak in detail when describing the Glover tower. Other stoneware bodies, as Guttmann's or the Bettenhausen balls or cones (p. 630), are equally used.

We mention also the stoneware apparatus of Kypke (Ger. P. 97208) and of the Friedrichsfeld ceramic works (Ger. P. 89025); *Fischer's Jahresber.*, 1898, p. 327.

The Rhenania works at Stolberg, when packing Gay-Lussac towers with cylinders alone, found that the stock of acid retained in the tower was not sufficient to provide for irregularities of work. They find it preferable to combine cylinders with coke packing, the former at the bottom, the latter in the upper part of the towers. If the pieces of coke are not too small, there is no stopping up by mud, and such a tower may go for many years (information received in 1902).

The Farbenfabriken Bayer (Fr. P. 421952 of 1910) overcome the difficulties of evenly distributing the absorbing-liquids in towers by substituting for the usual packing sections of filtering material, in the form of layers of sand, charcoal, etc. At the lower side of the filters a large number of points are arranged where the filtered liquid collects and drops on to the tray below. Vertical tubes are suitably arranged for the upward passage of the gases.

Other forms of lining and packing, which are equally applicable to Gay-Lussac or other towers will be described later on in connection with the Glover towers.

Plate-towers (*Lunge towers*).—An exceedingly suitable apparatus for this purpose is the plate-tower, described pp. 657 *et seq.* Lüty (*Z. angew. Chem.*, 1897, p. 485) gives reports from eleven various firms in Germany, Austria, England, America, and Russia, which have erected plate-columns as Gay-Lussac towers, and which are perfectly satisfied with the results. Niedenführ (*Chem. Zeit.*, 1897, p. 20) quotes reports from factories, showing that the loss of draught with plate-towers is much less than with coke-towers (only 1·5 mm.), and that the former, if combined with the latter, consume less nitre and produce more acid than coke-towers alone, especially by the equalisation of disturbances in the work.

A very good plan, where several sets of chambers are at work in the same factory, is to provide each set with a first Gay-Lussac tower in the shape of a "Lunge tower" and to convey the gases from all these into a large central coke-tower; the large quantity of weak nitrous vitriol employed in the latter is then employed for feeding all the plate-tower Gay-Lussacs of the individual sets (*cf.* p. 811, the Griesheim system of centralising the Gay-Lussac towers). In this case the action on the coke is altogether insignificant, owing to the low temperature and the slight amount of nitre to be dealt with in the central coke-tower.

A Lunge tower of 15 or 20 ft. does the same work as a much wider coke-tower of 30 or 40 ft., and causes only a quarter or a sixth of the loss of draught produced by the coke-tower (Niedenführ, 1902).

The combination of plate-towers and a large central coke-tower has the further advantage that any inequalities of work are thus rendered practically harmless, and the only real objection to plate-towers, viz., the small stock of acid which they contain, is thus completely avoided. As these towers are so low, it will be possible in most cases to place their tops at a slightly lower level than the bottom of the coke-tower and to feed them directly with the acid running from the latter without the necessity of again pumping up the weak nitrous vitriol.

By English acid-makers, coke-packing was for a long time, and is perhaps even now, preferred to all others, as shown by an enquiry made in 1900 by Messrs P. Spence & Sons (*Chem. Trade J.*, xxvii. p. 262); but their reasons are not very conclusive, and the just-mentioned firm has itself decided for an improved brick packing. No doubt some of the towers packed with bricks or cylinders have not answered their purpose, because the packing was too loose and nothing like as efficient for surface contact as coke-packing; but long experience has now shown that the latter, whose chemical drawbacks have been pointed out before, can be replaced by chemically indifferent stoneware, if moulded into proper shape ("Lunge plates," "Guttmann balls," etc.), and that in this way the towers can be made very much smaller than coke-towers, one-sixth to one-tenth or even less.

Repacking Gay-Lussac Towers.—Coke-towers, owing to the above-described circumstances, must be emptied and repacked from time to time. This must be done with great care, on account of the nitrous gas present in the towers, which is very poisonous. Since accidents have happened through gases remaining in the tower, official rules have been laid down in Germany, of which the principal points are the following:—Before repacking is commenced, the tower must be completely disconnected from the chambers, but the connection with the chimney must be left open. The tower must now be washed first with sulphuric acid, then with water or steam, until the liquid running off tests at most no more than 3° B. (1·022). During the taking out of the coke there must always be draught into the chimney: when unpacking from below the draught should act from the top; when unpacking from the top the draught should act from the bottom. If this cannot be done, the cover must be removed and a large hole cut in the side at the bottom. Towers packed with coke must be unpacked from the side and from without, in the case of tall towers on different levels. The packing-material must be immediately removed. The workmen must be provided with mouth-sponges, respirating-apparatus, india-rubber gloves, etc. Before removing the mud collected at the bottom it must be stirred up from without with water, and this must be repeated if nitrous vapours are evolved. Men suffering from lung- or heart-disease should not be employed in this kind of work.

The English Alkali Report, No. 31, p. 90, mentions a fatal accident which occurred in repacking a well-washed and unpacked Gay-Lussac tower, and which was evidently caused by the nitre-gas retained by the old brick-lining. It is therefore recommended to ventilate the towers in all cases from the top downwards during unpacking and repacking.

As an *antidote* against poisoning with nitrous vapours *chloroform* has been found to be very efficient (*Chem. Ind.*, 1904, pp. 296 and 379). The following rules for its application have been issued by the Rheinisch - Westfälische Sprengstoff Company. The person afflicted is to take 3 to 5 drops of chloroform, poured out of a drop-flask into a tumbler of water, once every ten minutes. The drop-flasks hold 0·5 g. chloroform, which is the maximum dose allowed by the German Pharmacopœia for a single taking; 1·5 g. = 3 drop-flasks being the maximum for a day. The weight of 3 drops chloroform is 0·045 g.; that of 5 drops, 0·078 g. According to Reusch (*Chem. Zeit.*, 1911, p. 289) strong and long inhalations of *oxygen* are preferable to the chloroform treatment.

Special rules have been officially laid down in Germany for repacking Gay-Lussac and Glover towers (*Chem. Ind.*, 1897, p. 365).

The *Chem. Trade J.*, published at Manchester, supplies posters for fixing up at chemical works, containing *Rules for Dealing with Dangerous Gases*, of which the following is an abridged abstract.

No person may enter a boiler, tank, drain, vitriol-chamber, or tower, except provided with a suitable respirator in good condition. If the gases cannot be absorbed, the men must be provided with a face-piece supplied with air or oxygen. They must be secured round the waist by a rope, and a man must be in attendance to render assistance if necessary. If a man is "gassed," he must be speedily removed into the open air, and placed in a warm, well-ventilated place. In bad cases an oxygen bottle (never to be used without a reducing-valve!) and lung exercise must be employed. If the man is conscious, the valve is very slightly turned on and the oxygen introduced into his mouth by a glass tube. If unconscious, the tube is put in one corner of the mouth, closing the lips round it and producing artificial respiration in the usual way; if the teeth are set, put the tube in one of the nostrils. The "lung exercise" (described in detail in the "Poster") is the same as that used in the case of accidents by drowning; it is not often necessary.

Complete Design of a Gay-Lussac Coke-tower.

In our second edition, pp. 520 to 523, a description and illustrations are given of a Gay-Lussac tower, as functionating at Frieberg many years ago. In lieu of this we shall here give a design of a modern coke-tower, as carried out by H. H. Niedenführ, Figs. 268 to 272. Fig. 268 is a sectional elevation, Fig. 269 another at right angles to it, Fig. 270 a sectional plan on the plane EF, Fig. 271 on the plane GH, on a scale of 1 : 100, and Fig. 272 a plan of the network below the saucer.

The tower stands on strong brick pillars (or else cast-iron columns), with an arched top. Above this follows a hollow network *x* of acid-proof brickwork, serving as cooling-channels for the wooden floor *z*, the outside of which is provided with the circular lead spout *y*, which keeps any acid running over away from the foundations. Six wooden uprights, *w w*, form the scaffolding for the leaden shell of the tower; they are tied at top and bottom by cross pieces, *v v*, forming a hexagonal frame. Cast-iron brackets fixed in *w w* support the lead sides of the tower, keeping these at a distance of 1 in. away from the wood.

The bottom of the tower is formed of a lead dish, *u u*, with a margin 6 in. high; this is made of lead 6 mm. thick = 14 lb. to the square foot. The sides and top are made of lead 3 mm. thick = 7 lb. to the square foot. The inside of the tower is lined at the bottom up to the top of the grate with 13-in. brickwork, above that 7 ft. high with 9-in. brickwork, above this 12 ft. high with 4½-in. brickwork; the remainder of the shell up to the top has no lining. The lining is everywhere kept an inch away from the lead.

The lead bottom is protected by thin acid-proof slabs. On these are erected pillars, *a*, *b*, which carry the stoneware grids, *c*, *d*, each consisting of three pieces, supported by the recesses of the pillars, as shown in the drawing. These bearers are 5 in. wide, 16 in. high, and leave open spaces, *e e*, between them, 7 in. wide. They are bridged over by the bricks, *g g*, which support the packing, formed of cylinders, to a height of 7 ft.

The cylinders (about which *cf.* p. 792) are placed as shown in Fig. 270, so that each of them stands on the crossing-point of four other cylinders. On the top of this packing there is a lead-covered cast-iron grid, *h h* (40 × 100 mm.), upon this 12 ft. high of coke-packing, then another grid, *i i*, and again nearly 12 ft. coke-packing. The top is formed by a shallow lead dish 5 mm. thick, 2 in. deep, with a number of acid "lutes," *k k*, sealed by small cups and fed from the long spouts, *l l*, which have as many lips as there are lutes to feed.

This tower is 9 ft. 4 in. wide and 41 ft. high within the lead; the inlet and outlet pipes are 25½ in. wide each.

Falding (*Min. Ind.*, vii. p. 691) gives a design of a Gay-Lussac tower which does not essentially differ from the above.

Both the inlet and outlet pipes of the Gay-Lussac should be provided with a contrivance for *the observation of the colour of the gas* before and after its passage through the tower—say, two glass panes placed opposite to each other; or a portion of each of the two pipes may be made of glass. The gas ought to be of a ruddy colour before entering the tower, and perfectly colourless after leaving it. It is a very good plan to make the "sight" in the shape of a narrow lead box, 6 or 7 ft. long, with glass panes at the opposite small ends. In this case the colour is seen through a deep layer of gas, and any admixture of yellow vapours is much more easily discovered than with the ordinary small sights.

Other Nitre-recovery Apparatus on the Same Principle as that of Gay-Lussac.

Instead of the Gay-Lussac tower in some works, but rarely in large ones, and altogether only exceptionally, absorbing-apparatus composed of *Woulfe's bottles* are used. Two different arrangements of this kind, which are quite obsolete now, are described and illustrated in our first edition, pp. 401 to 403.

More important than this are the proposals to retain the form of an absorbing-tower or column, but to make them in a cheaper or else in a more rational way than the ordinary large coke-tower. In our first edition (pp. 377 and 378) two such arrangements are illustrated, both of them consisting of stoneware pipes; but it is useless to repeat their description here, as they have not been practically tried or else act too imperfectly.

A very useful addition to Gay-Lussac towers, especially where they are not sufficiently large, was contemplated by the apparatus invented by F. Benker, and patented by the Soc. An. de Produits Chimiques de Javel (B. P. 10871 of 1884; Ger. P. 30749; *J. Soc. Chem. Ind.*, 1885, p. 456). A small lead tower is placed in the way of the gases before entering the ordinary

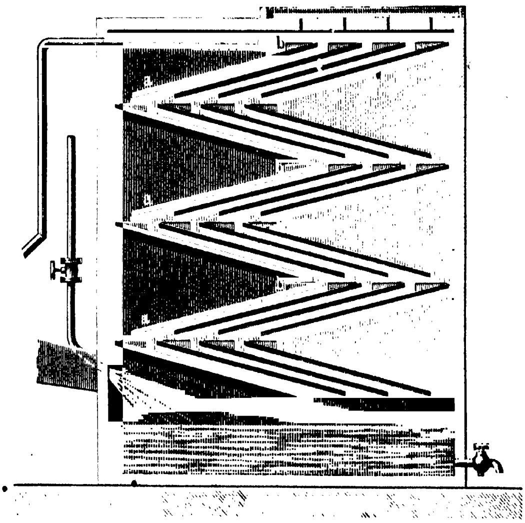


FIG. 273.

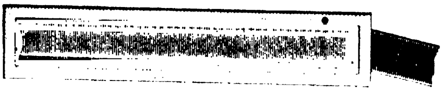


FIG. 274.

Gay-Lussac coke-tower. On its bottom there is a grid, covered with a little coke, merely to distribute the gases. On the top there are several spray-producers, of the shape shown on p. 752, Fig. 245, made of platinum, by which a fine rain of sulphuric acid is produced in the tower. The gases passing through it yield up a large portion of their nitrous acid, so that much less work remains for the Gay-Lussac tower to do.

This plan has been tried at several works, but with only moderate success. Probably the acid-drops fall down too quickly, before the gases have had sufficient time to act upon them.

The apparatus for absorbing gases by liquids, patented by Hoffmann and Carlisle (Ger. P. 48283), is shown in Figs. 273 and 274. It consists of a column or tower, fitted with groups of spouts, *a a*, inclined in opposite directions, in connection with overflow vessels, *b b*. This apparatus is also intended to make sulphuric acid from sulphur "evaporating" at the same time with nitric acid, both of them being forced into the apparatus by an injector, while the "spent gases" are forced back by another injector into the sulphur-chamber. It is not stated what material this apparatus is to be made of, and the very curious proposal for making sulphuric acid last described will suffice for judging of its technical value.

Very similar to this is the apparatus of Izidore and Biscons (B. P. 19907 of 1898; Ger. P. 106022), which contains inclined channels attached to the sides of a chamber through which sulphuric acid is run for the purpose of absorbing the nitrous vapours.

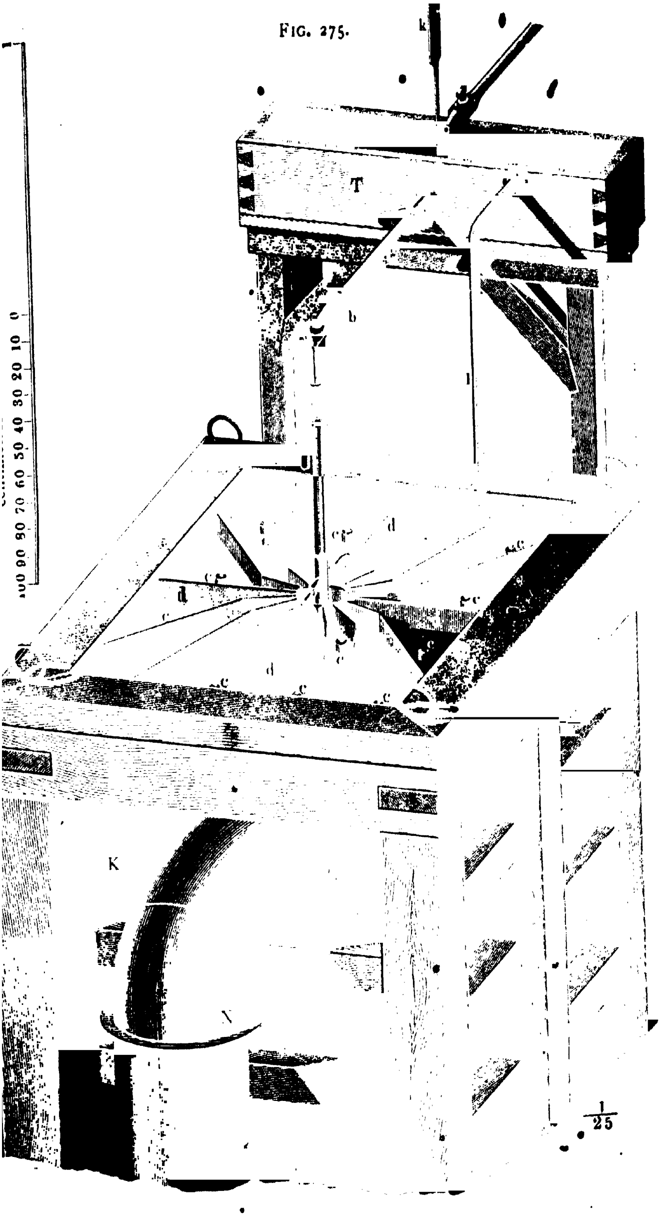
Distribution of the Feeding-acid.

For working the Gay-Lussac towers (as well as Glover towers, etc.) it is of great importance that the supply of sulphuric acid, which is to deprive the gases of their nitrous acid, be exactly regulated, and that from the beginning this acid be spread equally over the coke; otherwise too much sulphuric acid is used, and yet the gas may pass through the tower without giving up the whole of its nitrous acid. Special care must therefore be taken in the construction of the apparatus for spreading the acid. At one time this was performed by a number of small taps which evidently cannot be regulated for a very slight flow without danger of being stopped up, or by "tumbling boxes" and the like.

We shall first describe an arrangement for distributing the acid, which was originally applied at the Aussig chemical works by Mr Schaffner, namely the *acid-wheel*. In this the supply of acid is regulated by a single tap, which can be opened wide enough to prevent it from being so easily obstructed as the sixteen small taps in the former arrangement. Fig. 275 represents this apparatus on a scale of 1:25. In the top of the tower there are sixteen holes, *c*, through which the acid trickles on to the coke below. Each hole has an upstanding rim about 1¼ in. in height, which is covered by a lead cap, nicked at the bottom in a few places to the depth of ¾ in., so that the acid can pass through without hindrance. As soon as the top of the tower is covered with acid to the depth of that rim, the acid runs over into the inside of the tower; but no gas can escape through the holes, as they are luted with acid. The spreading of the acid is effected by a small reaction-wheel U, fed from the tank T by the tube *a* and the tap *b*, which regulates the supply. The lower part of the wheel and the two arms consist of lead; in this is fixed above a strong glass tube, and below another short glass tube, drawn out to a point which runs in a socket of glass or lead. One of the arms is also fitted with a glass tube, from which the acid runs out. There is a guide, consisting of two parallel rods of lead or of wood covered with lead, which rest on frames fixed in the holes *c c* of the top-frame, and on which four glass tubes are placed close to the upright column of the apparatus, so that they form a square within which the column revolves. As soon as the column is filled with acid the wheel revolves regularly, the liquid running out of the open arm. The quantity of the acid run in rules both the height to which the column is filled and the velocity of its revolution. The axle of the wheel is exactly in the centre of the tower; and a cylinder of lead about 4 in. in height is burnt to the top of the tower, so as to prevent the acid from getting to the centre. From this cylinder sixteen radial ledges, *d*, also made of lead and burnt to the top-lead of the tower, branch off at equal distances. These are continued in a straight line as far as the periphery of an imaginary circle, beyond which the wheel cannot discharge any acid, and then alter their direction; so that between each two of them one of the above-mentioned sixteen holes is placed. Thus the top of the tower is divided into sixteen compartments, each of which contains an opening for running off the acid, and all of which are fed by the wheel with an equal quantity of acid.

In England the spreading-apparatus is generally made

FIG. 275.



altogether of lead; we shall, further on, give a drawing of such a spreading-wheel in the description of the Glover tower.

Since it happens now and then that the reaction-wheel stops, especially with a small feed of acid, the arrangement of Seybel, at Liesing near Vienna, can be recommended, by which the wheel at each revolution strikes against a bell audible from below.

Even the best constructed acid-wheels are liable to get stopped now and then, and this sometimes causes a great deal of trouble if it is not at once perceived, as the tower then ceases to work properly and much nitre gets lost. Hence a new system has been pretty generally introduced, which works quite as well as the acid-wheels without a mechanical movement liable to get disturbed. It consists in running the acid into a vessel provided with a number of *overflows* kept exactly at the same level, each of these communicating with a separate pipe which leads the acid into the tower. This system can be carried out in a variety of ways, one of the best of which is shown in Fig. 276, as seen from above, Fig. 277 in transverse section, Fig. 278 in perspective view, with the sides partly cut away. From the top *a* the liquid runs into the central vessel A. The cover *b* is not exactly necessary, but is best provided, and is made loose, so that the interior of A is easily accessible. The cylinder A is nicked at the bottom, so that it communicates

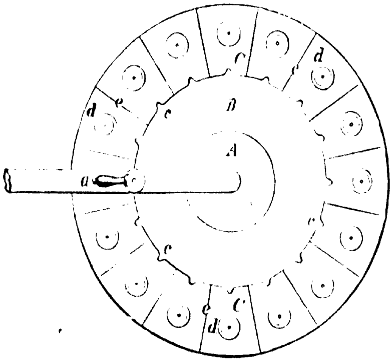


FIG. 276.

with the wider but lower trough B. This is provided all round its circumference with overflow-lips, *c c*, which may be close to

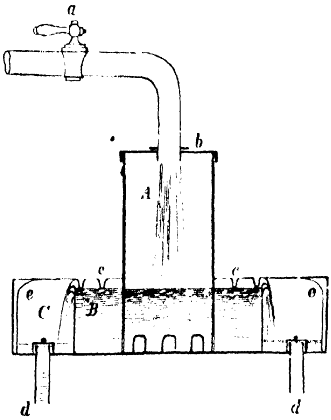


FIG. 277.

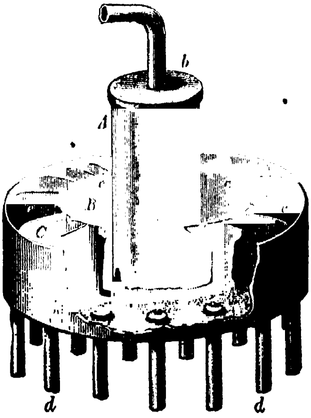


FIG. 278.

one another; sometimes 30 or 40 of these are made. They must be arranged in such a way that when B is once filled, all the overflows. *c c*. function precisely alike; this can be easily attained by dressing the lead of the lips a little up or down, as the case may be. Once right, they always act in the same manner. The trough B is surrounded by the wider trough C, which is divided into as many cells as there are lips in B. Each cell is independent of its neighbour; but the partitions, *e e*, are cut out on the top, so that, in case of the pipe of any one cell getting stopped up, the liquid overflows into the next cells. Each cell is also provided with a separate pipe *d*, made tight in its bottom, and hydraulically sealed either there, as it is shown in the diagram, or else on or within the tower. The whole is generally, in the case of Gay-Lussac towers always, made of lead, but it may also be made of earthenware, iron, or other material suitable for any special case.

Brieglеb (Ger. P. 10386) has constructed a distributing-apparatus consisting of a cone made of regulus metal, on the top of which a jet of acid is directed. The upper part of the surface of the cone is plain, but the lower part is fluted, so that the acid is distributed into a number of jets which are caught in a circular vessel surrounding the base of the cone, and are separately carried away by pipes. No doubt this apparatus can be made to work properly, but it is much less easily kept in order than the simple overflow apparatus shown on p. 802.

In the case of towers of great horizontal section, where the number of pipes coming from the distributor is inconveniently large, much may be saved by employing only one pipe to every four holes on the top of the tower, each pipe ending over a small trough placed at the point of intersection of the lines connecting these four holes; these small troughs will then empty their contents simultaneously into all the four holes. Of course the same precautions have to be taken for securing an equal flow into all the four holes as mentioned in connection with Figs. 276 to 278.

A very ingenious, but somewhat complicated distributing-apparatus, in which a mechanical revolving drum is employed, is described in the patent of Brock and Saye (No. 11492 of 1885; *J. Soc. Chem. Ind.*, 1886, p. 487).

Hommel and the Metals Extraction Corporation (B. P. 19668 of 1908) describe a special form of the apparatus for dividing the acid in Gay-Lussac or Glover towers.

Klute and Ising (Ger. P. 209276) place between the acid-tank and the distributing apparatus a float-valve provided with several outlet pipes, which can be shut off separately, so that in case of altering the supply of acid each pipe is opened entirely and cannot be stopped up by foreign bodies, which easily takes place in the case of partially opened valves.

The action of a column (whether it be a Gay-Lussac, or a Glover tower, or a hydrochloric-acid condenser, etc.) is, of course, all the more efficient the more uniformly the feeding-acid is distributed over its whole area. It is equally self-evident that towers of a large horizontal section require more feeding-places than narrow ones. It may be laid down as a general rule that there ought to be no smaller number of distributing-pipes than one to each superficial foot of the cover of the tower; but this is a minimum which is greatly, and no doubt advantageously, exceeded at many works.

Another way of dividing the feeding-liquids for absorbing, condensing, and reaction-towers is described by the Farbenfabriken vorm. Fr. Bayer & Co. (Ger. P. 241767). They employ layers of a porous material, like sand, powdered coal or metals, or plates, rods, small tubes, etc., of a porous material, like burnt clay, sintered quartz, porous cement, etc., through which the liquid sinters and is made to drop off at suitably arranged edges or points. By changing the grain, the porosity and the thickness of the porous layer, as well as the height of liquid on the dividing plates, the velocity of feeding can be regulated at will.

The *regularity of the supply of acid* to the coke-tower is of the utmost importance for its good working. The whole acid-chamber process is so constituted that its course must be kept as continuous and uniform as possible, and the large bulk of the lead chambers in this case serves as a regulator, similar to the air-vessel of a blowing-engine, so that the gas, on leaving the chamber, issues, or at least ought to issue, with nearly absolutely uniform speed and composition. In similar intervals of time there will therefore be a similar quantity of nitre-gas leaving the chambers; and this in the absorbing-tower should always find the same quantity of acid, lest either there be an escape of nitre-gas or the nitrous vitriol come out too weak. But if the acid flows out of a tank, the opening of the tap remaining the same, the flow will be much quicker at the beginning, when the tank is full, than afterwards, when it is partly empty, and the tower will thus be fed very irregularly. The speed of outflow of liquids decreases in the proportion of the square roots of the heights of liquid in the tank ; for instance, when the tank is filled to the height of 4 ft., the flow of acid will be twice as fast as when it only stands 1 ft. high—both being cases which often happen in practice.

In order to secure a very regular supply of absorbing-acid to the tower, several arrangements have been adopted—for instance, Mariotte's vessel (p. 709) or the apparatus shown in Fig. 279. The vessel Z is placed with its mouth downwards in an open basin E, in such a manner that its mouth is luted by the acid contained in the basin ; therefore nothing can run out of Z. But as the acid runs away from E through the pipe *b* on to the coke-tower, the level of E is lowered, the mouth of Z becomes free, a few air-bubbles enter, and acid flows out till the original level is reached, and the mouth of Z is luted again. The valve *d*, with the valve-rod *c* passing through a stuffing-box, serve for closing the mouth of Z during the time that this vessel is being fed through *x*.

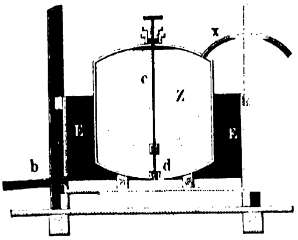


FIG. 279.

In a simpler shape the same principle used to be applied a number of years ago in a few English alkali-works, as shown in Fig. 202, p. 531 of our second edition, under the name of "vacuum retorts," which have been abandoned as being too troublesome to keep in order. Very efficient is the *balancing-apparatus*, Fig. 280, A is the large acid-tank on the top of the coke-tower, made of wood lined with lead, which is filled from time to time. Beside it stands a lead cylinder B of equal height and 12 in. wide; the two communicate at the bottom through the lead pipe *a*. This pipe ends in A with a valve-seat *b* of hard lead, bored out in a taper shape. In this plays a ball-valve *c*, also made of hard antimonial lead ("regulus"), which is continued below into a small guide-rod, and above into the lead-covered iron rod *d*, which projects above A, and is suspended by a short chain from one arm of the balancing-beam *e*.

The latter swings with its centre on a steel edge *f*, and carries on its other arm, exactly over the cylinder B, another chain, from which a leaden bucket *g* is suspended inside B. Acid is poured into the bucket *g* until it sinks to a certain depth in the acid standing in B; by pouring in more or taking out some of the acid in *g* that depth, and with it the height of acid in B itself, can be regulated at any time: this bucket is therefore a form of float, preferable to the solid lead float figured by Schwarzenberg. The bucket *g* is so weighted, and the length of the chain such, that at a certain height of acid in B the valve *c* must close the opening *b*. The valve *c* with the rod *d* and its chain is about as heavy as the float *g* along with its chain, and closes the opening *b* so long as a portion of the weight of *g* is neutralised by the upward pressure of the acid in B. As soon, however, as the cock *h* begins to run and the float sinks down, the rod *d* is raised by means of the beam *e*, and the ball-valve *c* leaves the opening *b* free; thus acid flows across into B through *a*, lifts the float *g*, and *c* sinks down into its position, closing *b* again. Thus, by small oscillations of *e*, always the same quantity of acid will run out of B in the same time, as this only

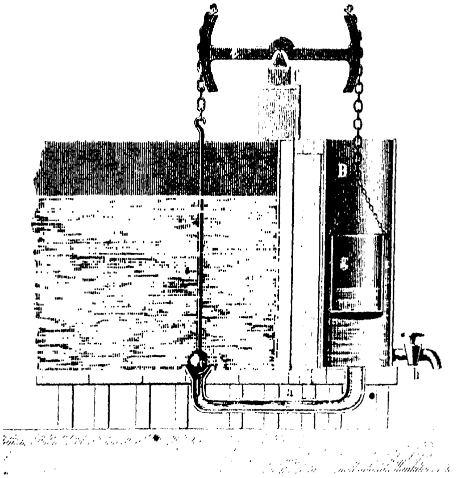


FIG. 280.

depends on the weight of *g* and the length of the chain, but is independent of the level of the acid in A. The ends of the beam *e* are shaped as segments of a circle, in order (by means of the chains) to convert their circular movement into a rectilinear one for the rod *d* and the bucket *g*.

The above apparatus, as formerly figured in other books and as employed in many factories, does not work well, and has even been given up in many places where it had been erected. In the first place, the beam is usually represented swinging on a pin which passes through its centre; but then the friction is very great and soon becomes greater by the iron rusting, so that the beam sticks fast. This cannot happen if the arrangement is that shown in the above diagram, viz., a steel edge like those of delicate balances; when strongly plated with nickel it remains free from rust. But, above all, the valve *c* ought not to be a truncated cone, as it is generally represented, but it should be ball-shaped. The guiding by the arc-shaped arms of the beam is not so absolutely vertical that a conical valve could not now and then jam itself in its seat during its play upwards or downwards; in that case the apparatus ceases to work. If, however, the valve is ball-shaped, a slight deviation from the vertical does no harm, as the ball always closes the hole, and jamming fast is out of the question. Whilst those manufacturers who had erected the above-mentioned imperfect apparatus were mostly induced to give it up again on account of its constantly breaking down, the arrangement figured here works with the greatest ease and regularity and can be highly recommended. At some of the largest works, from not being acquainted with the *right* way of making the apparatus, they have abandoned automatic regulation altogether, and leave it to the workmen to set the running-off tap of the acid-tanks according to the level of the acid—a very rude method, which, according to the explanation just given, there is no reason for retaining.

(Whenever "lead-covered" iron rods are mentioned, it should be understood that for this purpose the iron rod is put into a pressed lead tube of convenient bore, and both ends of the latter are soldered up.)

Fig. 281 shows a new kind of acid-tap introduced by Ernst March Söhne at Charlottenburg, constructed entirely different from the usual way. The central part consists of stoneware, and is connected with the two end pieces made of antimony-lead, by means of screw-bolts. The plug of the tap is firmly pressed down by means of a metal screw on the top, so that there can be no leakages, but the plug can be loosened when stuck fast. It is claimed that these taps combine the advantages of metal and stoneware taps.

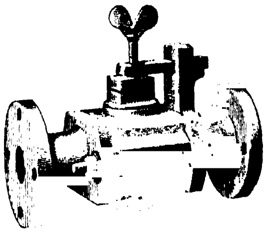


FIG. 281.

Some works employ for regulating the rate of feeding the contrivance shown in Fig. 282, which is interposed between tap *a* and the central vessel A in the apparatus, Fig. 278. The liquid runs from *a* into a leaden box, divided into two compartments, D and E. D communicates with E by the four pipes, *f*, *g*, *h*, *i*, placed at different levels, and the lip *k*; E is at the bottom provided with a wide outlet-tube *l*. According to the width to which tap *a* is opened, box D will be more or less filled; with the strongest feed the acid will run into compartment E out of all four pipes and the lip *k*; with a smaller feed fewer of the pipes will come into action. Supposing the attendant to be instructed to work with three pipes, he will have to see that the acid runs out only of *f*, *g*, and *h*, the pressure being almost constant at the level of *h*. This, of course, is greatly preferable to regulating the

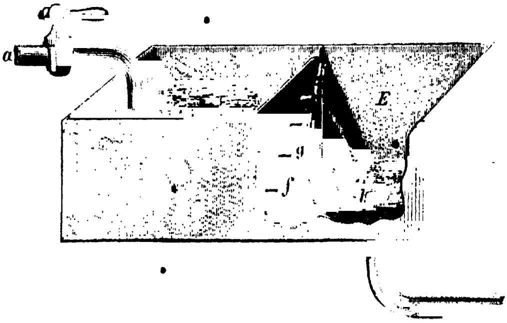


FIG. 282.

position of tap *a* by mere rule of thumb, and it operates independently of the level of acid in the main reservoir to which tap *a* belongs. This contrivance acts very well.

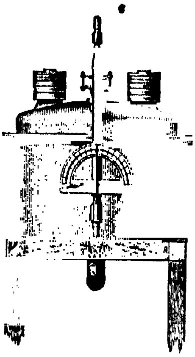


FIG. 283.

Wild's apparatus, called "Semper idem" (made by the Vereinigte Thonwaarenwerke, Charlottenburg), realises a completely uniform velocity of outflow by means of a siphon floating in the liquid, so that the difference of level between both arms of the siphon remains always the same. The outer arm carries an index fixed to the plug of the tap, by means of which the speed of outflow can be made to vary at will. The first rough regulation is produced by a ball-valve. All this is made clear by Figs. 283 and 284*a* and *b*.

Where the *pulsometers*, to be described below, are introduced, probably one of these is provided for each kind of acid: Glover-tower acid, Gay-Lussac acid, chamber-acid. In this case no special regulator for the pressure of outflow is required if the air-cock of the pulsometer is only opened to such an extent that the apparatus can work day and night without pumping up too much acid. The acid-tanks on the top of the towers are once for all filled up to a proper height and are kept at this by the play of the pulsometer with unimportant change of level.

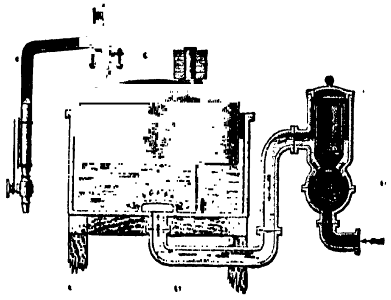


FIG. 284*a*.

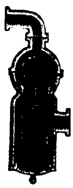


FIG. 284*b*.

Centralised working of the Gay-Lussac Towers.—The following very perfect system is followed at the Griesheim works. Seven sets of chambers are employed, each possessing ordinary Gay-Lussac towers; the whole of these communicate with a large common tower, of a horizontal section of 10×30 ft., which receives the fresh acid of 142° Tw., divided into 480 jets. The resistance in this tower amounts to $\frac{1}{12}$ up to $\frac{1}{8}$ in. of water. The weak nitrous vitriol formed here is pumped up and feeds the ordinary Gay-Lussac towers. Since these require variable quantities of acid, this is divided among the seven towers by an acid-wheel having seven chambers of variable dimensions, formed by slightly inclined movable spouts resting on the partitions between the chambers. By shifting these spouts backwards or forwards, the time of feed and also the quantity of acid serving each compartment can be varied at will. From each compartment a pipe conducts the acid to one of the Gay-Lussac towers, where it is again subdivided in the ordinary way. (In the same works there is a similar arrangement for dividing the strong nitrous acid, chamber-acid, and nitric acid among the seven Glover towers, placed at a considerable distance from the central office.) Figs. 285 to 288 illustrate the above. Fig. 285 shows the acid-wheel, supported by the glass bulb α, floating in a vessel filled with sulphuric acid. This avoids all friction, so that the wheel never stops. The glass point β and a short piece of tubing at the bottom form one of the guides; a thimble δ, just below the funnel, constitutes the other guide. We notice the seven compartments *a*, *b*, *c*, *d*, *e*, *f*, *g*, and the spouts γ (Fig. 288), which can be moved backwards and forwards, and thus admit of dividing the supply at will. Thus, for instance, in Fig. 288, which represents a section through all the seven compartments (projected on a straight line), we find that the acid is divided among the six compartments *a*, *b*, *c*, *e*, *f*, *g* in the proportion 7, 7, 7, 8, 5, 8; *d* receives nothing, because the set of chambers to which it belongs is standing still.

At Griesheim the nitrous vitriol is thus brought up to a strength equal to 60 g. $NaNO_3$ per litre, and the total consumption of nitre has been brought down to 0·83 per 100 H_2SO_4. This system allows of keeping one of the sets with an excess of SO_2 (which is very good for concentration in platinum), since

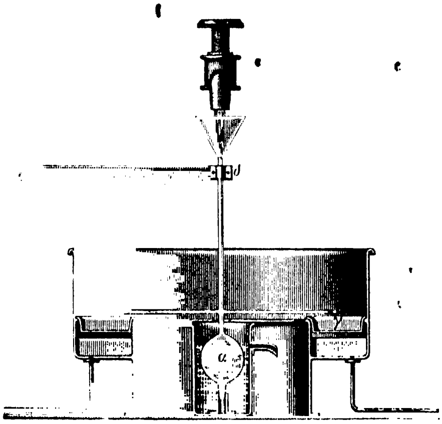


FIG. 285.

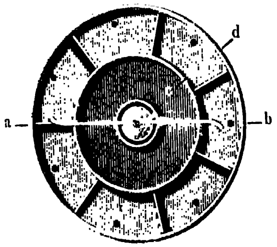


FIG. 286.

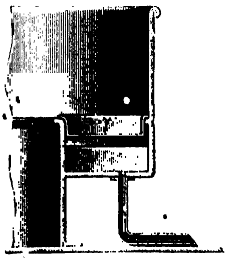


FIG. 287.

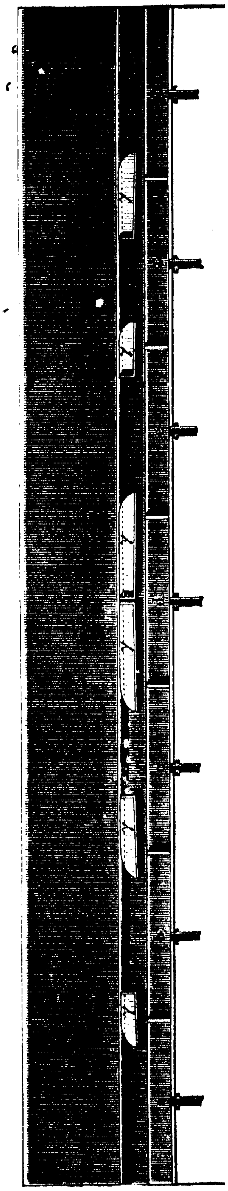


FIG. 288.

the exit-gases from this system are neutralised by the gases of the other sets in the central tower.

Pumping-apparatus for Acid.

It is rarely possible to feed the acid-tank on the top of the absorbing-tower with concentrated vitriol by natural fall; where the concentration takes place in the Glover tower, that possibility is excluded from the outset. There is therefore need for an *apparatus to force the acid up to the top of the absorbing tower;* the same apparatus will also serve for forcing the nitrous vitriol and the chamber-acid to the top of the denitrating tower. Ordinary force-pumps cannot be employed here, because these cannot be made without using metals which are acted upon by the acids, at least not for such quantities as have to be treated in this case. Fortunately, we have two metals which resist the sulphuric acid very well, viz., cast iron and lead, and with the aid of these an apparatus can be constructed in which the force-pump acts only indirectly, viz., through the compression of a column of air, which thus enters into the forcing-apparatus proper and conveys the acid to any desired height.

The ordinary plan of working (introduced about 1838 by Harrison Blair) is this, to convey air compressed by an air-pump or, more properly speaking, by a small blowing-engine into the pressure-apparatus, above the surface of the acid, exactly similar to the way in which every chemist in his wash-bottle forces the liquid up in the outlet-tube by blowing air in through another tube. In this proceeding there is no special limit of height, so long as the apparatus is made strong enough to resist the pressure, and the air-pump is sufficiently powerful.

The air-pumps are generally constructed in this way:—The steam-cylinder and the air-cylinder are both fixed on a common horizontal ground-plate, or cast in one piece with the same; they are then worked by a common piston-rod with a piston at each end. A cross-head sliding between motion-bars gives the necessary guidance; and a pretty heavy fly-wheel secures regular action. The dimensions of the pump are chosen according to the size of the works; for a set of chambers of from 140,000 to 200,000 cub. ft., a steam-cylinder of 8 in. diameter, an air-cylinder of 12 in. diameter, and a stroke of

18 in., with from 40 to 60 revolutions per minute, suffice for pumping all the nitrous vitriol, concentrated acid, and chamber-acid. The compressed-air pipe in this case has 1¼ to 1½ in. bore. Much care has to be taken of the valves of these pumps: if they work with too much noise, they last only a very short time; but, in any case, a second pair must always be ready for putting on when the first give way. At the works formerly managed by myself, I sent the exhaust-steam of the engine into the steam-pipe for the chambers, the steam-boiler belonging to which worked at only 10 lb. pressure per square inch; thus the steam for pumping the acid was got for next to nothing, since only the difference of pressure before and behind the steam-cylinder had to be made good by consumption of fuel. [*Cf.* p. 723. This description was given in the first edition of this work (1879), and is therefore much prior to the very similar proposal of Sprengel, B. P. No. 10798, of 1886.]

The air-pipe, which must be made of very strong lead tubing, is not conducted direct from the air-pump to the pressure-apparatus, because in that case acid would inevitably be squirted back into the air-cylinder and soon ruin the valves; but the air-pipe is carried upwards a distance of from 10 to 13 ft., and then as much downwards, before entering the acid-vessel. Close to the air-cylinder a small branch-tube with a cock is soldered on, in order to let out the air when the pumping is finished. Sometimes there is also a pressure-gauge fixed to it: but this is not of much use; for, in the first place, it is soon destroyed by the violent oscillations at every stroke of the piston and by the acid fumes; and, secondly, the workman can judge much more conveniently than by looking at the gauge, from the noise of the pump and the valves, whether it works easily or heavy—that is to say, with much or little pressure.

The acid-vessel serving as pressure-apparatus is made in various forms. Originally (and even now in many places) it was made in the shape of a soda-water bottle, as shown in Fig. 289, afterwards as a horizontal cylinder (Fig. 290) with bolted-on covers; but it is now more usually, as shown in Fig. 291, a horizontal cylinder with one semicircular and one neck-shaped end, the latter closed by a manhole door. These vessels are called "acid-eggs." The vessels like Fig. 289 are usually lined with lead; those like Figs. 290 and 291 usually not. Experience has everywhere shown that it is needless to protect the cast iron of the acid-egg by a lining of lead; even the nitrous vitriol and the chamber-acid act so little on cast iron that such a protection becomes unnecessary.[1] I have found an acid-egg after five years' continuous use for all three kinds of acid in entirely good working order. Lining with lead has this drawback, that as soon as a little air gets between the lead and the cast iron through the smallest possible chink the lead is driven away from the iron in many places, and its protecting action becomes quite illusory, whilst the contents of the egg are diminished. *Dilute* acids are best pumped up by means of stoneware acid-eggs, as supplied by the Vereinigte Thonwaarenwerke, Charlottenburg, or by stoneware pulsometers.

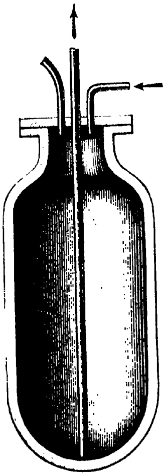


FIG. 289.

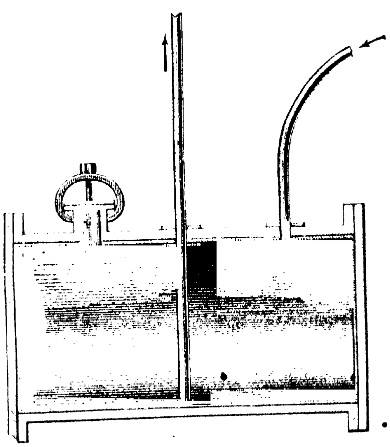


FIG. 290.

The horizontal has several advantages over the vertical shape:—first, that no well is needed for the acid-egg, which may lie on the floor and thus is accessible all round; secondly, that in the case of excessive pressure, the weakest part (viz. the manhole) being situated sideways, the acid squirting out is not so likely to injure men and machinery as in the case of squirting out vertically, especially if the cylinder is placed with the manhole turned away from the machinery.

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[1] It has been noticed that the acid-eggs made by some foundries are liable to crack after a few months' use, while those supplied by other foundries, and made like ordinary metal castings, last much longer. With acid-eggs from the Widnes foundries, cracking is asserted never to take place when they are used for sulphuric acid, but only when used for mixtures of sulphuric and nitric acid. According to private information, it is preferable to line the acid-eggs in any case with lead.

In Fig. 291, A is the acid-egg, whose walls are 2 in. thick;

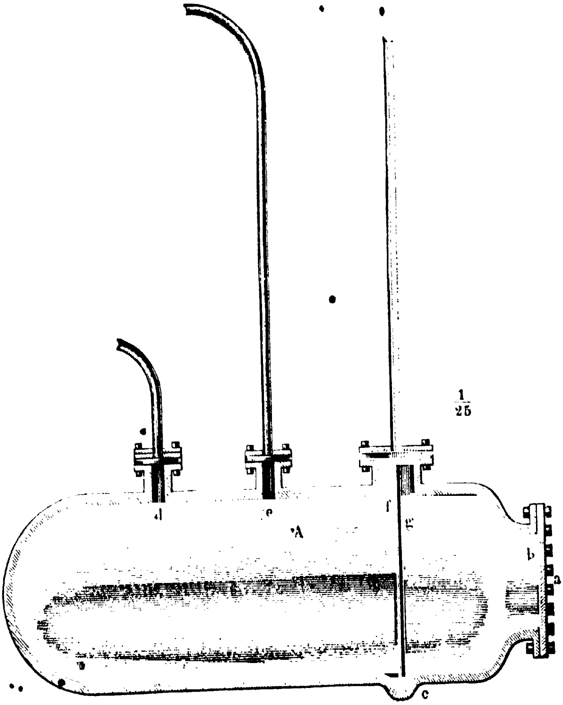

Fig. 291.

b is the neck, with the manhole lid *a* fixed to it by bolts and nuts[1]; a thick india-rubber washer makes the joint tight; *c* is a recess at the bottom of A, into which the delivery-pipe *g* projects, in order to expel the contents of A as completely as possible; *d*, *e*, and *f* are three branch-pipes—*d* for introducing the acid, *e* for the air-pipe, and *f* (the widest of them) for the delivery-pipe. The pipes have each a strong lead flange soldered to it, which rest on the flanges of the branches, *d*, *e*, *f*; by putting loose iron washers on the top, and screwing all three together by bolts and nuts, the joint becomes perfectly tight. The inlet branch *d* may be left open, and closed after each filling by a small plate bolted on; but in most cases there is an *inlet valve* for the acid, of the shape shown in Fig. 292. (The plain stoppers with lever-rods, figured in Muspratt's *Chemistry*, cannot stand any great pressure.) A and B are acid-tanks, which need not be placed so close to the pressure-valve C as they are represented in the diagram. C is a cylinder of strong lead, about 10 in. wide, whose top is on a level with the top of the tanks, but which is deeper than these, so that they may communicate with C through the pipes *a* and *b*, connected with their bottoms. *a* and *b* end in the bottoms of the tanks with valve-seats of "regulus" metal, and are usually closed by taper valves with long lead-covered handles: no pressure upon these is exercised from below, and therefore they need not be provided with any special contrivance against this. When it is necessary to run the contents of these two tanks, or that of a third tank, not visible in the diagram, but similarly communicating with C, into the acid-egg, the respective bottom-stopper is taken out, the bottom-valve *c* in C also remaining open. The latter valve, which must be very well ground into its regulus seat, communicates through the pipe *d* with the corresponding inlet branch of the acid-egg. On the top it is connected with the lead-covered iron rod *e*, which ends above in a screw-worm e_1, and can be turned by means of the hand-wheel *f*. A very strong iron frame, *g g*, with a female thread corresponding to the worm e_1, is bolted to the bottom-joists, *i i*: both the timber and the iron rods must be very strong, as there is a good deal of strain upon them in screwing the valve in and out. As the cylinder C is equal in height to A and B, it can never run over; and when the acid in C stands at the same level as that in the tanks, the valve *c* is screwed down tight by means of the hand-wheel, the corresponding stopper is put into its seat in the tanks, and the air-pump is started. The whole pressure of the acid, which has sometimes to be lifted to a height of 100 ft., will then act from below on the valve *c*; and unless the latter has been screwed down perfectly tight, the acid will squirt out violently. Although, with a little care on the part of the workman, this should never happen, yet several accident caused by men being splashed with acid have led to providing the cylinder with a cover and a stuffing-box, *k*, through which the rod *c* passes; the splashing then does no harm, as the acid cannot get out. At the same time the stuffing-box serves as a guide for the valve-rod, which would otherwise have to be provided in some other way. Sometimes (not always) there is a small pipe provided for taking any acid squirted out into one of the three tanks. In this way the same acid-egg can serve for pumping strong acid, nitrous vitriol, and chamber-acid out of their respective tanks one after another.

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[1] Some manufacturers propose to construct the acid-eggs without manholes, as these may render it difficult to keep the joints tight, but the metal-casting must be much more difficult to make in this case.

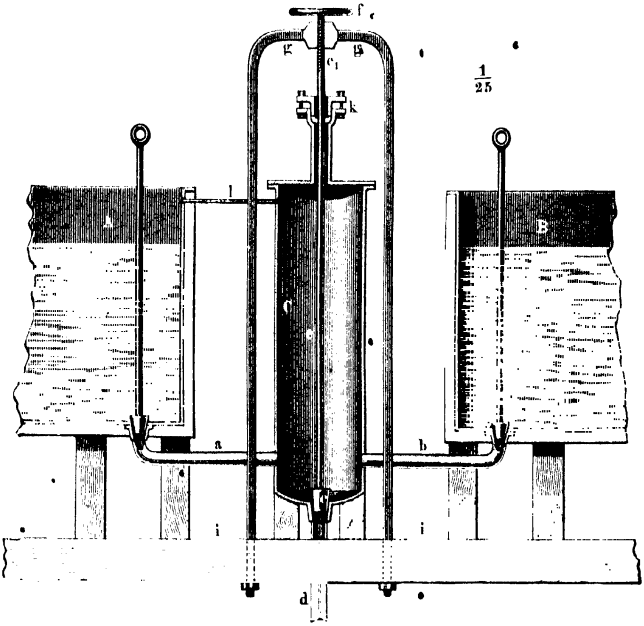


FIG. 292.

A self-acting apparatus for filling the acid-eggs, constructed by Mr Harrison Blair, which, Mr Mactear says (*J. Soc. Arts*, 1878, p. 558), works well, is shown here according to the description in Richardson and Watts' *Chemical Technology*, vol. i., part v., p. 217. A (Fig. 293) is a strong cylinder of lead closed at both ends [probably cast iron would be preferable]; B a valve-box, and C a delivery-pipe, into which the pipe D enters a little above the vessel. D is continued to E, where it passes to the inside of the vessel, and F joins D at the lowest part. G is the pipe which brings the air from the pump. So long as D contains no liquid, the air from the vessel will pass through, and by thus preventing any pressure on the liquid in the vessel, it will be filled through the valve-box. When the vessel is full, the egress of the air through F being stopped by the liquid, the latter will be forced up E (being lower than F), which, acting as a siphon, fills D and effectually stops the passage of air. As the pressure of air increases, the liquid rises up the delivery-pipe and is conveyed to any required point, while the liquid in D falls with the level of that in the vessel, until this sinks below the bend in D, when the air rushes through, carrying with it all the liquid out of D. This leaves a free passage for the escape of air during the time the vessel is again being filled, the air-pump working the whole time.

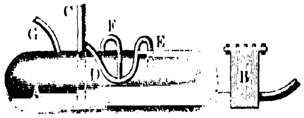


FIG. 293.

At the Rhenania works the rod *c* of the inlet-valve *c* (Fig. 292) is coupled with the air-cock on the acid-egg in such a way that when the egg is full the attendant cannot by mistake shut the air-cock first, but is obliged to screw down the valve *c* before he can shut the air-cock and open the connection with the air-pump.

An automatic acid-egg air-valve is described in *Chem. Trade J.*, xvii. p. 82 (*J. Soc. Chem. Ind.*, 1895, p. 749). The acid entering the egg tends to raise a wooden float, and this lifts a valve connected with the air-tap. When later on the compressed air forces the acid out, the float descends and the air-supply is automatically shut just as the last acid is being driven out.

As soon as, in the ordinary kind of apparatus, the pumping is finished, the air-pump, to which now no resistance is offered, begins all at once to go extremely fast, and by its noise draws the attention of the workman to the necessity of stopping it. Directly after, the air-cock in the pipe conducting the compressed air to the acid-egg is opened. Nevertheless some compressed air accompanies the last portions of the acid and rushes vehemently out of the top of the delivery-pipe; and in order to *prevent the acid from splashing about* a special contrivance must be adopted, for instance that shown in Fig. 294. A leaden cylinder, open at top and bottom, stands within the tank A; it is jagged out at the bottom in a few places; and the holes *a a* higher up also help to give free communication between B and A. Also the top of B is cut out pretty deeply in a few places (*b b*). Within B the perforated plate *c* is suspended by a few lead strips, *i i*; the whole is covered by a loose cover, *d d*, which is kept at a little distance from the top of B by the lead strips, so that the air can escape between them. *d* has a flange of 8 in. depth; in the centre it carries a short tube, *e*, to which the "regulus" cock of the delivery-pipe *h* is burnt. Since it is extremely difficult to keep such a cock tight, especially under great pressure, it is surrounded below by the pipe *g*, which also fits into *d*, and thus carries away the droppings. This contrivance acts in the following way:—When the acid forced up through *h* arrives at the top, it runs through *f* and *e*, then through the sieve *c* and into the cylinder B, whence it easily passes through into A. But in the last stage, when compressed air arrives at the same time with the acid, the latter cannot be squirted

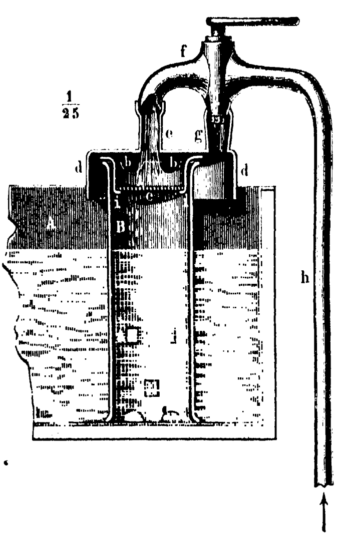


Fig. 294.

about, nor can the current of air act upon the surface of the acid within the tank so as to splash it about; for it is broken by the sieve *c*, and escapes through the openings of *c* and the annular space below *d* without doing any damage; the acid accompanying it runs quickly down through the sieve *c*. The cock *f* and the pipe *g* are required only when a single acid-egg has to feed several tanks placed, at a considerable distance apart, for instance one on the absorbing-tower and two on the Glover tower; for then the delivery-pipe must be divided into two parts, and each must be provided with a stop-cock, only that leading to the working tank being open. If, however, the tanks to be filled are placed close together, no cocks are required, but the simpler arrangement, Fig. 295, can be employed, which may also be made much smaller than (for the sake of clearness) is here indicated. Within the same lead-lined box A there is a special compartment, B, constructed by means of a lead partition, *a*, and cover, *b*. The side of B is jagged out at the bottom at *c c*, in order to communicate with A. The delivery-pipe fits into the cover *b*; the air rushes against the sieve *e* and escapes out of the pipe *f* without doing any harm. In the bottom of A there are three valve-seats, *g*, *h*, and *i*, connected with as many pipes leading to different tanks; but only one of the valves is left open at a time; the two others are

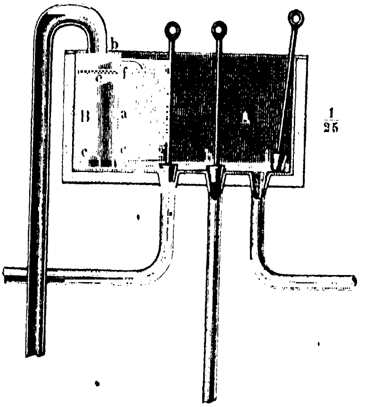


FIG. 295.

closed by plugs, and the tanks communicating with them therefore receive nothing.

In smaller works there is usually only one acid-egg, which serves for pumping all the strong acid, nitrous vitriol, and chamber-acid, one after the other. In this case the air-pump has nothing to do during the time that the egg is getting filled from one of the tanks; if the cubic contents of the chambers do not exceed 200,000 cub. ft., there is time enough for that. But where the chamber-space is larger, two acid-eggs, at least, will be required, of which one usually serves for the strong acid and nitrous vitriol, the other for the chamber-acid; in this case the same air-pump can do all the work if the air-delivery pipe is provided with two branches and two stop-cocks, one of the eggs always getting filled whilst the contents of the other egg are being pumped up; the air-pump is thus fully utilised.

Johnson and Hutchinson (B. P. 8141, of 1885) describe a combination of three upright vessels, so connected that the compressed air contained in one is always utilised in the next, and is not lost, as in the usual process.

A somewhat different kind of acid-lifting apparatus is Laurent's pulsometer. It is made of cast iron for sulphuric acid with lead pipes (Figs. 296 and 297), and of stoneware for hydrochloric or nitric acid (Fig. 298). In the former case the joint between the cover *a* and pan *b* is best made good by a lead washer, in the latter case by an india-rubber washer; *c* is the manhole, with the rising-main *d* and the pipe *e* for compressed air. The rising-main *d* has a side connection with the swan-neck pipe *f*. The feed-pipe *g* is connected with the store-tank *h*; the latter must be fixed at such a height that even when the pulsometer is quite full, and *h* nearly empty, there is still a greater head of liquid on the pulsometer than the length of pipe *f*. The clack *i* (which may be replaced by a ball-valve or by a Bunsen valve, as shown in Fig. 298) prevents the acid from being driven back into *h* whilst rising in *d*. Pipe *d* must be fixed in such a manner that it can be taken out together with pipe *f*, in order to attend to the latter.

The play of the apparatus is as follows:—The acid runs from *h* through *g* into *b*, during which time the air, continuously being forced in through *e* from the air-pump, escapes through *f* and *d*. As soon as vessel *b* has been filled to the upper opening of *f*, the air cannot escape very well, and a little pressure ensues. In spite of this, through the momentum of inertia, the acid rises still a little, arrives at the top of the siphon (at *k*), and causes this to act, whereupon the level of the liquid in all the pipes becomes that of the outlet of *f*, that is *m*. As the air

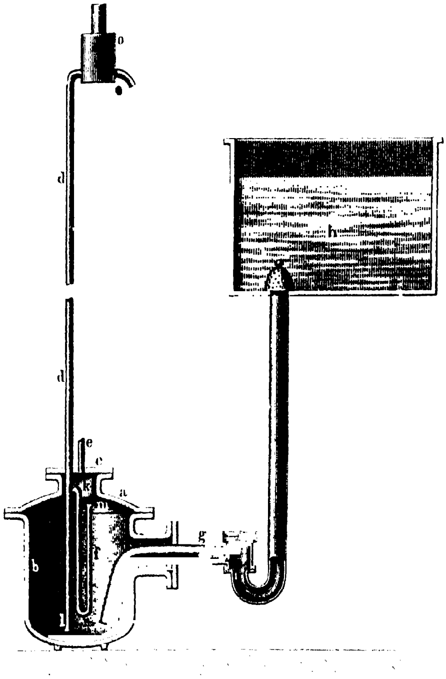


FIG. 296.

cannot now escape, the pressure gradually gets up and the liquid rises in pipe *d*, but sinks in vessel *b*. As the pressure on the surface of liquid in *b* must be the same at all points, and each point has also to bear the counter-pressure of the column of liquid in *d*, the acid must sink exactly as much in the outer limb of *f* as in the vessel *b*, and the level must at last arrive at *n*. Now as the column of liquid between the lower end *l* of pipe *d* and the upper outflow at *o* is still rather higher than that from the lowest point *n* of the siphon to the outflow at *o*, the air must throw the acid from *n* out of *o*, the pressure within *b* must cease, and the vessel *b* must be filled again from *h* through *i* and *g*. Even if a little acid had accidentally run back from *d* into *f* and filled the siphon, this would not prevent the filling of *b* from *h*, since this tank (as we have seen above) is placed high enough for this purpose.

If during the forcing up of the acid the outflow from *o*, owing to the friction in *d*, were not so great as corresponds to the volume of air entering at *b*, strong pressure will ensue on the surface of the liquid in *b*, and at last the acid in siphon *f* would be forced to point *n* before the outer level in *b* had sunk to that

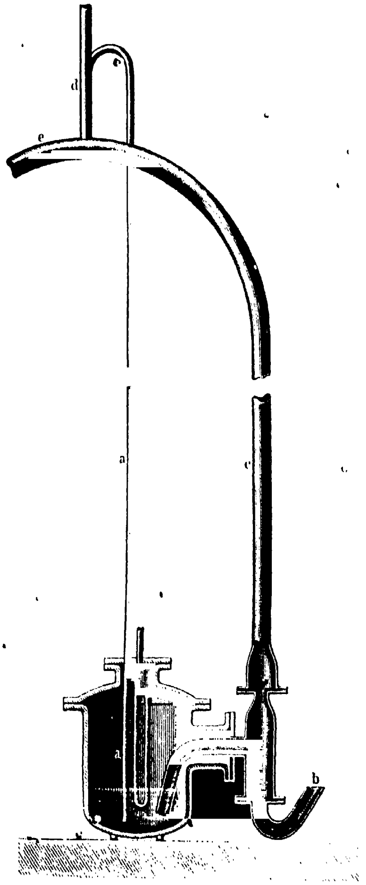


FIG. 297.

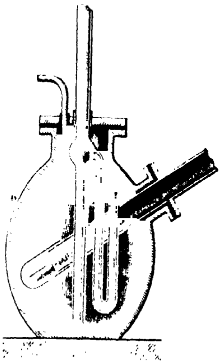


FIG. 298.

point. Then the air will bubble up through *n* into *d* and out of *o*, and will keep the liquid column suspended. This bubbling can be perceived when the ear is put close to *d*, and can be remedied by closing the air-pump cock a little, and afterwards regulating the pressure in the following way:—In the air-pipe *c*, which is $\frac{1}{4}$ of an inch wide, a flanged joint is made between the cock (not shown here) and the cover *c*, in which a copper disk is placed, perforated with a pin-hole (say $\frac{1}{24}$ in.). If in case of the cock being quite open this hole is still too wide, so that the air, instead of lifting the acid, bubbles through *d*, the pin-hole is narrowed to the required extent so that in future the tap may be opened fully whenever the apparatus is to act. It can then go on for many years without any supervision, unless the valve *i* gets obstructed by impurities.

Since, during the time *b* is getting filled, the air escapes without being utilised, it is best to place the tank *h* at least 5 ft. above *b*, and make pipe *g* very wide, so as to shorten the time of filling. The compressed air must always be under the same pressure, and the air-pump must therefore have a regulator of some kind. The pin-hole in the regulating-disk must be arranged for the highest pressure which may be expected.

It is possible to lift liquids to a greater height than corresponds to the pressure of air present, by placing a second pulsometer midway up the height to be overcome, and regulating both pulsometers so as to act together. Above all, valve *i* must be kept in order; for strong sulphuric acid it must be made of lead (regulus metal), and very carefully; for chamber-acid or hydrochloric acid it may be made of india-rubber.

This apparatus, once properly set, acts day and night without any supervision; it is started or stopped in a moment by opening a tap.

Fig. 296 shows a pulsometer of 50 l. total, and 40 l. available space; the rising-main must be 1$\frac{3}{8}$ in. wide; in the case of a wider pipe part of the acid would run back and air would rise up. The apparatus can act thirty times per hour, and lift 25 to 30 cb.m. (say 875 to 1050 cub. ft.) per twenty-four hours. Fig. 297 shows an apparatus intended for greater speed; there is a rising-pipe, *a*, of 1 to 1$\frac{3}{8}$ in. width, provided with a valve, and a much wider feed-pipe, *c*, also provided with a valve. The latter must always be full; the outflow thus takes place under the pressure of the liquid column *d e*, and therefore very quickly. Fig. 298 shows the form best adapted for stoneware vessels, which should stand a pressure of 4 atm.

Simon (*Z. angew. Chem.*, 1890, p. 356) describes a combination of two similar pulsometers which utilises the compressed air otherwise escaping during the filling of the vessel, the apparatus being connected by a Y-pipe and automatic ball-valve.

The principle of the pulsometer has been improved by replacing the siphon by a float-valve and most thoroughly worked out by Paul Kestner, of Lille, London, and Berlin. His pulsometers are illustrated and described in our vol. ii., 2nd ed., pp. 408 *et seq.*; in the present volume we have also shown, on p. 259, a Kestner's pulsometer as constructed for nitric acid. Most chemical works now employ these apparatus, and speak very highly of them; many works have abolished the acid-eggs entirely in favour of Kestner's pulsometers.

At Freiberg, in 1902, Kestner pulsometers (which are still doing very good work) were in use, as well as real pumps. One kind of these is made of antimonial lead ("regulus metal") with valves of phosphorus-bronze, another consists of a cast-iron barrel, lined inside with lead, with a porcelain ram and phosphorus-bronze valves. The former serves only for pumping up to 33 ft., the latter up to 80 ft. (25 m.) by means of a 10-in. conduit. Both these and the Kestner pulsometer, which is used for the Gay-Lussac and precipitating towers, give entire satisfaction.

In the *J. Soc. Chem. Ind.*, 1903, p. 337, Kestner discusses various systems of automatic acid-elevators, and in *Chem. Zeit.*, 1910, p. 734, he describes a special form of his pulsometer with back-suction for hot gases and for high pressures.

Guttmann (*J. Soc. Chem, Ind.*, 1903, p. 1333) greatly recommends Frépont's emulsifier, described in *Z. angew. Chem.*, 1903, p. 915.

Recently Kestner has greatly improved his pulsometers, the new shape of which he styles: "Panzer Säure-Pulsometer" (armoured acid-pulsometers). Model A, shown in Fig. 299, is made of cast iron for use with strong sulphuric acid or caustic liquor; for weaker sulphuric acid it is lined with lead. The acid runs from the tank A, placed at an elevation, through valve

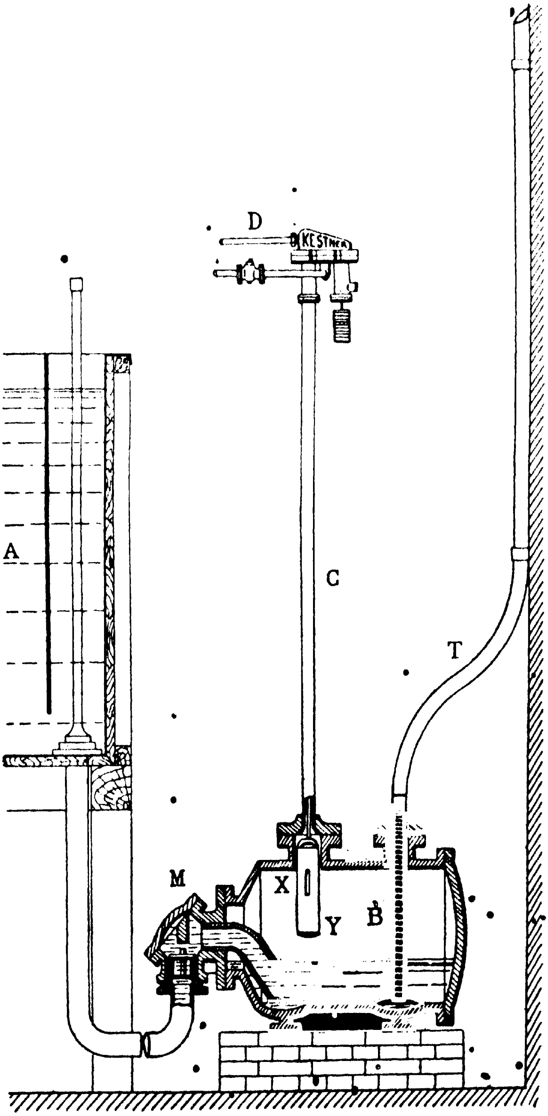


FIG. 299.

M into the pulsometer B. When this is filled, the acid lifts up the float X, whereby the rod C opens the inlet-valve in the air-distributor D and shuts the outlet-valve, so that the air forces the acid upwards in pipe T. Part of the compressed air at last enters into T; owing to the ensuing diminution of the pressure the float descends and opens the air-outlet, the air-inlet being shut. Thus the force-pipe T can be left without a valve, which greatly increases the safety of the apparatus and the simplicity of working it. For use with hydrochloric acid the pulsometer is lined with ebonite, or it is made of stoneware, like the pulsometers for nitric acid. Model B provides for the case that the spent-air must be separately conducted into the open air, *e.g.* when pumping fuming oil of vitriol, solutions of sulphur dioxide, etc., and for feeding filters, spray-producers, or similar purposes. This form is shown in Fig. 300. The platinum wire A, passing through an acid-proof stuffing-box, carries the float C, and on its upper end causes the turning of the pulley E, which works the stoneware tap F so as to admit or shut off the air.

Mr Kestner states that his new pulsometers are used in most German and Austrian acid-factories. Altogether 7000 of his pulsometers have been sold.

Automatic acid-elevators are also made by the Deutsche Steinzeugwarenfabrik in Friedrichsfeld (Ger. Ps. 145599 and 145600), as described in *Chem. Ind.*, 1905, pp. 432-433.

The firm Paul Schütze & Co., at Oggersheim (Pfalz), manufactures automatic acid-eggs of a special construction which have stood the test of many years' practical experience. They are described in *Chem. Trade J.*, 1905, xxxvi. p. 90.

Plath has constructed an automatically acting acid-egg, supplied by the Deutsche Ton- und Steinzengwerke at Charlottenburg (Ger. P. 159079). In *Z. angew. Chem.*, 1907, pp. 1186 *et seq.*, he describes several modifications of it.

Some improvements in apparatus for raising liquids by air-pressure are described in the B. P. 10051, of 1907, by Scherb.

C. Simon, of Stolberg, has constructed a pneumatic acid-pump, provided with an automatically acting piston-governor, which is stated to be superior to the regulation by floats in various respects. *Cf.* also Plath on mechanical means for raising acids, *Z. angew. Chem.*, 1902, p. 1311.

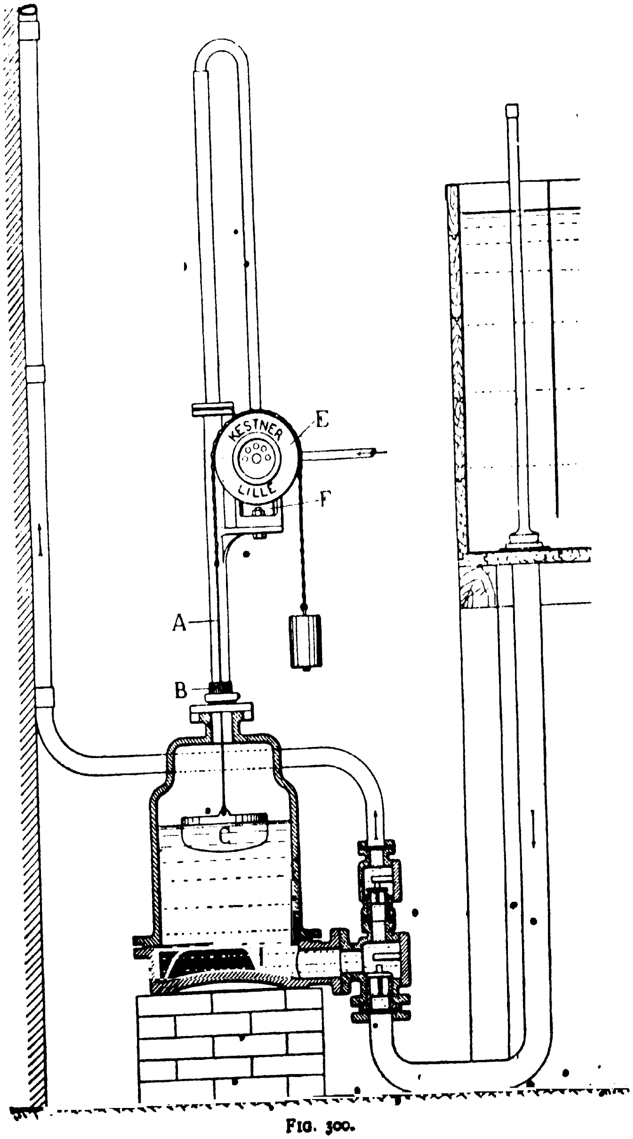


FIG. 300.

Th. Meyer (*Z. angew. Chem.*, 1919, pp. 1556-1559) shows that the waste of power in raising the acid by compressed air is enormous; the effect produced represents only 2·4 per cent. of the theoretical 71 per cent. of the motive power consumed in a sulphuric-acid factory is required for the raising of acid by compressed air, at a cost of 5·67 pfennig per 100 kl. acid 50° Bé. It is therefore an important task to find out a cheaper way of attaining the desired result, and this Meyer claims to have done, in the shape of a *centrifugal pump* ("Turbo-pump"), made of antimony-lead, built by the firm Sächsisch-Anhaltische Armaturenfabrik at Bernburg. He calculates the useful work of this pump = 19·4 per cent. of the theoretical, that is, eight times as much as that required for the acid-egg system, and a cost of only 0·71 pfennig per 100 kl. acid. He claims also some other advantages of his pump against the acid-eggs, viz., (1) less wear and tear of the acid-conduits, since there are no violent shakings by the air, but quite even work; (2) from the same reason, less loss of power in the rising mains; (3) automatic working, without an attendant; (4) no escape of nitrous gases, which is unavoidable when raising nitrous vitriol by compressed air; (5) less cost of plant.

The Badische Anilin- und Sodafabrik (Ger. P. appl. B60169) employs for their acid-eggs an automatically moving governor-tap, which is set into motion by a mercurial differential pressure-gauge.

A review of the recent progress in the construction of automatic apparatus for raising liquids by compressed air is given by Deimler in *Chem. Ind.*, 1911, pp. 39-46.

We now pass on to the construction of *tanks or reservoirs* for sulphuric acid (much of which will apply also to hydrochloric and nitric acid). *Open* reservoirs for sulphuric acid are always made of lead, usually in the way shown in Fig. 292 and elsewhere, viz., a strong wooden frame to which the lead sides are fixed by means of straps, turning the upper edge over the top, just as in the construction of chambers, or else a box made entirely of wood with lead lining; in each case the thickness of the lead need not exceed 5 or 6 lbs. per superficial foot, if the wood frame is so constructed as to take all the side thrust; but it is preferable to use thicker lead, say 9 or 10 lbs., on account of wear and tear. Where it is intended that the acid run into the tank in a hot state should cool therein, the tanks are much better made circular in shape, of much thicker lead (say 10 lbs. or more), and strengthened on the outside with strong iron hoops, which may be connected by strong cross-stays in the case of very large tanks. Considering the increase of pressure from the top downwards, the binding-hoops should be placed nearer together in the lower part of the tank.

Even *brickwork* may serve for acid-tanks (sulphuric, hydrochloric, nitric acid), if the bricks, tiles, stones, etc., are acid-proof. Volvic lava is the best material (*cf.* later on). The mortar in this case should be that described on p. 149, viz., a paste made of asbestos powder and silicate-of-soda solution, with or without some other solid admixture, as barytes, etc. This mortar should at first not be brought into contact with water, which would dissolve out the sodium silicate, but at once with acid, which causes silicic acid to be separated in the solid state and to render the joints perfectly tight.

For *closed tanks* for sulphuric and strong nitric acid the best material is *iron*, either cast or wrought iron, as may be most suitable for constructive purposes; and this material is also adapted even for *pipes*, etc., in cases where no air can enter, whose moisture might dilute the acid.

Working the Gay-Lussac Tower.

After the above explanations but little need be said as to the working of the absorbing-tower. The following points have to be observed in this respect.

The *gas* entering the tower must show a distinctly red colour in the "sight"; on the other hand, the exit-"sight," behind which a board painted white ought to be placed, should show a perfectly colourless gas. The gas escaping from the top of the tower, or of the chimney connected with it, ought not to produce any considerable amount of red vapours when it meets the outer air (see below). Furthermore, the chamber-gas before entering the tower should be as *dry* and as *cool* as possible, lest the absorbing-acid be diluted or heated. For this purpose the last chamber receives very little, sometimes even no steam, so that its acid remains at about 106° Tw.; moreover the gas is often conducted through a long pipe or a tunnel, or into a shallow box with several vertical partitions, where it has to move backwards and forwards. In these cooling-apparatus water may be applied outwardly to assist the cooling, especially in summer-time. Sometimes the bottom of the box is covered with strong vitriol, in order to dry the gas; this, however, to a certain extent, only anticipates the tower. Hartmann and Benker (*Z. angew. Chem.*, 1906, p. 136) employ a tubular cooler for the same purpose. The *sulphuric acid* serving for absorption must show at least 144° Tw.; but this is only a minimum, which ought to be exceeded if possible; acid of 148° absorbs much better, that of 150° or 152° Tw. better still; wherever possible, acid of 152° Tw. should be employed for the absorbing-process. Such acid can be got without any difficulty from the Glover tower—not quite so easily from pans placed on the top of the pyrites-burners, where the acid rarely gets beyond 144°. Schwarzenberg even proposed to use acid of 170° Tw., because it absorbs three times as much as that of 144°; but this is out of the question, owing to the large additional cost of concentrating from 152° to 170°.

Above everything, care must be taken that the acid used for absorbing is as *cool* as possible. Hot acid absorbs very badly; much nitre is lost, and at the same time a weak nitrous vitriol is produced. Bornträger (*Dingl. polyt. J.*, vol. cclviii. p. 230) goes so far as to suggest cooling the acid down to 5° C., but it is hardly possible to go to that length. In fact, at the French works they believe that 25° is the best working temperature. It is therefore necessary either to provide a very large tank for cooling the acid concentrated in pans or in the Glover tower before it is used in the Gay-Lussac tower, or else (as the cooling by mere exposure to the air is a very slow process, especially in summer, and in large works enormous tanks would be required for it) special cooling-apparatus is employed. As such many works use double spouts—an outer one filled with water, and an inner one, in which the hot acid travels. In this case it is rarely possible to apply the rational principle of running the cooling-water in a current opposite to that of the acid to be cooled, because, on account of the length of the spouts, there is no fall for this. Such double spouts also have a disagreeable tendency to swell out at the bottom whenever a little more pressure takes place, because the lead when hot diminishes in strength, which in any case is not considerable.

This drawback can be avoided by the arrangement sketched in Fig. 301, viz., by attaching to the spout, at about every 30 ft. of its length, a tube rising perpendicularly from the double bottom through the upper spout and bending over the side of the latter; the water can issue out of this, in case of stronger pressure, without mixing with the acid. The upright tube also serves for the escape of the air-bubbles which are often contained in the water, and which may stop the stream as well as cause the spout to bulge out.

FIG. 301.

On pp. 551 to 553 of our second edition a tubular cooling-apparatus is described and illustrated, to which we merely refer here as it is now obsolete.

A simpler but perfectly efficient cooling-apparatus is found in most German works. The acid runs out of the Glover tower immediately into a cylindrical trough of thick lead, about 2 ft. high and wide, and runs out of it again through a pipe coming away sideways from its bottom and turned upwards. In the trough there is a narrowly wound lead coil or even two such coils, through which cold water is continually running from below; getting heated in the bottom part of the coil, it rises up and is taken away hot at the top. The cooling here generally goes down to 40° C., and is supplemented by letting the acid stand in tanks; but 30° to 35° C. might easily be attained. This is a very rational method of cooling, because the hot acid running in at the top comes into contact with the upper, hot part of the water-coil, whilst the acid ultimately flowing away from the bottom, which is already cooled down to a great extent, is cooled still further by the cold water in the bottom of the coil. There is also no trouble caused by any deposit forming in the acid, if there is a sludge-valve provided in the bottom of the trough.

At some works I have seen a good cooler which I describe from notes supplied to me by Dr Stahl. A flat pan, say 30 ft. long, 5 ft. wide, and 6 in. deep, made of wood and lined with 6-lb. lead, is divided lengthways into ten narrow channels by leaden strips, 4 in. wide and 6 in. apart. Each strip stops alternately 6 in. from the ends of the pan, so that a zigzag channel is formed, into which a 1-in. or 1¼-in. lead pipe is laid, forming a coil of 200 ft. in length. The acid runs through the zigzag trough, and cold water in the opposite direction through the lead pipe. Where the hot acid enters, a double loose lining, made of 4 ft. length of heavy 2-in. pipe, cut open lengthways, is put into the trough in order to protect it; this piece must be renewed about once every six months, and if this be observed the trough will not require any repairs for many years. A cooler of the above-stated dimensions suffices for cooling 18 tons of hot Glover-tower acid down to about 30° C. every twenty-four hours.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 300) describes a cooling-arrangement practically identical with that described here; and he gives details concerning its function. The acid travels altogether about 1000 ft., and its temperature is brought down from 139° or 149° C. to 28° or 39° C. Further on (p. 304) he contends that such cooling is unnecessary (except, perhaps, in order to save the lead from quick corrosion), on the strength of laboratory experiments in which acid of sp. gr. 1·75 did not absorb the nitrous vapours from chamber-gases much less at 100° than at the ordinary temperature. But as he never went beyond 0·47 or at most 0·69 per cent. N_2O_3 in the acid, his statements are not to the point. We know from experiments made on the nitrous-acid tension of sulphuric acid that this increases rapidly with the percentage of N_2O_3, and in all cases with the rise of the temperature. In case of such low percentages of N_2O_3 as those employed by Crowder, the tension of N_2O_3 is not very great even at higher temperatures; but in actual work we must aim at higher percentages of nitre, in which case any higher temperature of the acid would act injuriously. This has been fully confirmed by observations communicated by Hasenclever (*Chem. Ind.*, 1893, p. 337). A high temperature not merely prevents the absorption of N_2O, but even expels it from stronger nitrous vitriol.

At large works the two systems of cooling just mentioned are sometimes combined. I consider as perhaps the best plan a perpendicular cooler, similar to that which has been adopted at several coal-tar works for cooling benzene vapours (described in detail and illustrated in Lunge's *Coal-Tar and Ammonia*, 4th edition, fig. 184, p. 726); that is, two short, cylindrical or square boxes, one above the other, connected by a very large number (50 to 100) of narrow, perpendicular pipes, about 2 ft.

long and $\frac{1}{2}$ in. wide, the whole standing in a wider tank supplied with cooling-water. Hot acid is run into the top box, slowly finds its way downward through the thin pipes, which possess a very large cooling-surface, and arrives cool in the bottom box, whence it rises up in a special pipe and is run off almost on a level with the top box. The bottom box must be provided with a sludge-valve. Or else the acid is contained in the outer tank, and cooling-water is run through the system of boxes and pipes just described.

Very efficient cooling might be produced by the action of a current of air, either by forcing this through the hot acid, or else by running this down a tower in which air rises up by the action of a fan-blast or by chimney draught; but where very large quantities have to be treated, the supply of cooling-air might require too much power to be economical.

In ordinary circumstances the absorption in the Gay-Lussac tower requires *at least* one-half of all the acid produced. This is obtained from the Glover tower without any other cost but that of pumping up; in the case of other denitrating apparatus the cost of concentration has to be added to this. Frequently the necessary quantity of absorbing-acid is stated at a lower figure—for instance, as one-third of the whole production; but this in most cases is certainly insufficient, and no doubt a large loss of nitre would result from it. On the other hand, manufacturers working with Glover towers, who, apart from the trifling expense of pumping, have no concentrating-expenses at all, send all their acid once a day through the Gay-Lussac tower. This is quite right. Bode (*On the Glover Tower*, p. 49) calculates that with a loss of four parts of nitre or 1·75 of N_2O_3 to 100 parts of acid of 170° Tw., the absorption requires at least 56 per cent. of *all* the acid of 144° manufactured, if very strong nitrous vitriol (with 1·75 per cent. of N_2O_3) is to be obtained. Such strong nitrous vitriol, however, is not obtained in ordinary working; and therefore considerably more than 56 per cent. of all the acid manufactured must be run through the Gay-Lussac tower in order not to lose any nitre. In fact, some manufacturers send much more than their daily make through the Gay-Lussac towers; but at some of the best-conducted works they manage with about $\frac{4}{6}$ or $\frac{5}{8}$ of the daily make. Of course, everything depends upon the style of working the chambers. With the ordinary style, where there is about 20 cub. ft. of chamber-space to each pound of sulphur burnt in twenty-four hours, the above-quoted figures are quite sufficient; but the forced or high-pressure style of work, where there is not much more than half the just-mentioned chamber-space (pp. 639 *et seq.*, and below), cannot be kept up except by a very large floating capital of nitre, and in this case twice or more the daily production of acid has to pass through the Gay-Lussac tower. I am acquainted with two very large English works (belonging to the same firm) in which the quantity of acid run down the Gay-Lussac towers is from three to four times the daily make; and in this case the ordinary chamber-space of 20 cub. ft. is allowed. But it seems doubtful whether such an enormous feed of the towers is advantageous (apart from the cost of pumping), considering the action of the coke on nitrous vitriol (pp. 350 and 791). At other works I have found $1\frac{1}{4}$ or $1\frac{1}{2}$ times the daily make of acid run through the Gay-Lussac tower, and so forth.

At Greisheim they employ 65 per cent., at Stolberg (1902) about 200 per cent. of the daily make of acid for working the Gay-Lussac tower.

Sorel (*Traité*, p. 312) supplied a Gay-Lussac tower at one of the St-Gobain works with 39,000 l. acid of 60° where the chambers produced 2·75 k. H_2SO_4 per cb.m., with 45,000 l. for a production of 3·0 k., with 52,000 l. for 3·5 k., and with 62,000 l. for the "high-pressure" production of 4 k. per cubic metre. In every case the average consumption of nitre was 0·8 k. for 100 k. H_2SO_4, or 2·45 k. for 100 k. sulphur burned. [This statement differs very much from the figures by Mr G. E. Davis (*suprà*, p. 640), according to which the consumption of nitre was much greater in the case of high-pressure work, but even as regards the easiest work it was much higher than the consumption attained by Sorel at high-pressure work.]

Heinz and Petersen (Ger. P. 217723) assert that sulphuric acid of 54° to 56° Bé. can absorb about four times as much nitrogen oxides as acid of 60° Bé., and is therefore much better adapted for use in the Gay-Lussac. This avoids the necessity of further concentrating the acid coming from the Glover, which only requires cooling before being used in the Gay-Lussac, where it absorbs the nitrous gases extremely quickly and without getting heated, so that there is much less danger of loss than in the present way of using more highly concentrated acid. The denitration is also easier, since the nitrous vitriol does not require diluting, and this is also done more quickly than up to now.

[These assertions must be reproduced here with all reserve, as they are in complete contradiction to all experience made up to now.]

The specific gravity of the *nitrous vitriol*, as the acid issuing at the foot of the Gay-Lussac tower is called, does not differ very much from that of the acid fed in at the top. In the usual case, where there is ample chamber-space and the sulphuric acid is almost entirely condensed in the last chamber, the mixture still necessarily present in the exit-gases is, of course, absorbed by the stronger acid in the Gay-Lussac tower, and the nitrous vitriol running out at the foot is then 1° or even 2° Tw. weaker than the feeding-acid. But in the "forced style" of working (p. 639) there is a considerable quantity of acid contained in the exit-gases in the shape of mist, which is retained in the Gay-Lussac tower, and, added to the nitroso-sulphuric acid absorbed, may make the nitrous vitriol even a little stronger than the feeding-acid.

When properly treated, nitrous vitriol ought to be very little coloured, and should have only a slight smell of nitrous acid; but on being diluted with water, especially hot water, it ought to effervesce strongly and give off thick red vapours. At some works this rough test is considered sufficient for judging of the quality of the nitrous vitriol; but at all the better works it is tested in the laboratory, which can be accomplished in a very short time by the permanganate method (*cf.* p. 387). Now and then this test should be supplemented by testing in the nitrometer, in order to make sure whether any nitric acid is present or not. By these testings it can be seen from day to day whether the percentage of nitre increases or decreases. In the former case, if the other tests of the chamber-process agree with it, this is an indication that some of the nitre must be taken off; in the latter case this test will, better than any other, show, before any damage has been done, that more nitre is required. In any case nitrous vitriol should not contain less than 1 per cent. of N_2O_3; above 2½ per cent. it is too strong, and there is danger of nitrous gas escaping without being absorbed, which can be controlled by the colour of the exit-"sight." In this case more strong acid must be charged at the top; and if there is an excess of nitre-gas in the chambers, a little less nitre must be used.

The Gay-Lussac acid, or nitrous vitriol, is essentially a solution of nitrososulphuric acid ("chamber-crystals") in sulphuric acid. Formerly it was believed that it regularly contained some nitrogen peroxide or nitric acid (Winkler, Kolb, Hurter, Davis, etc.); but this assertion was only caused by the imperfection of the then employed analytical methods, as shown for Winkler's and Kolb's results by myself (*Chem. News*, vol. xxxvi. p. 147), the nitric acid being produced during the analyses themselves. The contrary fact, viz., that *ordinary* nitrous vitriol contains no appreciable quantity of nitric acid, was first proved by me; and it has been confirmed by several subsequent investigators. This is even the case when so much nitre has been introduced intentionally, as in Lunge and Naef's experiments, or by inadvertence, that the last chamber contains some nitrogen peroxide (*Chem. Ind.*, 1884, p. 10). It has been shown before (pp. 350 and 791) that this is no doubt due to a reduction of the nitric acid, originally formed from the nitrogen peroxide, by the coke packing of the Gay-Lussac towers. In the case of columns filled with a non-reducing packing probably nitrous vitriol containing nitric acid would be much more frequently met with; but with coke-towers, and with the ordinary style of working formerly employed in all works, it is one of the signs of the regularity of the process if *no* nitric acid occurs in the nitrous vitriol. Probably it is different when working with the "high-pressure" style (p. 639), where the chambers are made to turn out nearly twice as much as before, by supplying them with a comparatively enormous quantity of nitre (without, however, losing more of it in the long run, owing to correspondingly large Gay-Lussac towers). In this case it follows most distinctly, from Lunge and Naef's observations (next Chapter), that there must be a *large* quantity of nitrogen peroxide in the last chamber, too large to be completely reduced by the coke to N_2O_3, so that the nitrous vitriol will be found to contain some nitric acid.

A very strange error existed for many years, both in all publications on the subject, and in the ideas of nearly all those practically concerned in the manufacture of sulphuric acid who gave any attention to the chemistry of the subject. This error is: that nitrogen peroxide, N_2O_4, forms only a "loose" combination with sulphuric acid of such concentration as is employed for working the Gay-Lussac tower, and that, therefore, very little N_2O_4 is absorbed in that tower, unless it can be there reduced by SO_2 to N_2O_3. This erroneous assumption, coupled with another error, viz, that the "nitre" in the chamber exit-gases consists essentially of N_2O_4, and the *true* observation that the "nitrous vitriol" generated in the Gay-Lussac tower does not contain anything but N_2O_3, has led to the invention of Brivet, Lasne, and Benker (Ger. P. 17154), who introduce into the exit-gases, on their way between the last chamber and the Gay-Lussac tower, a certain quantity of burner-gas, by means of a steam-jet. The excess of moisture thus imparted to the burner-gas is removed by means of a small coke-tower fed with Glover-tower acid, and the gas is now mixed with the chamber-gases before entering the Gay-Lussac tower. It was supposed that the nitrogen peroxide would thus be reduced:

$$N_2O_4 + SO_2 + H_2SO_4 = 2SO_2(OH)(ONO).$$

No doubt this would be really the case if an appreciable quantity of "free" N_2O_4 did exist in properly composed exit-gases; but this is not so, at least with the ordinary, not "forced" (high-pressure) work. I have, moreover, conclusively proved (*Berl. Ber.*, 1882, p. 488) that there is no foundation for the assumptions underlying the above-mentioned patent, more especially the idea that N_2O_4 did not easily and completely dissolve in sulphuric acid of 142° Tw. In fact the first favourable reports upon the practical success of that patent process have not been confirmed by subsequent observations, and it must be held that for properly-managed chambers the process offers no advantage.

Benker has several times reverted to proposals, founded upon the alleged difficulty of absorbing N_2O_4 in the Gay-Lussac tower, by introducing SO_2 at some place where it is to reduce N_2O_4 to N_2O_3; he has, however, found that this cannot be done in the Gay-Lussac tower itself, and he therefore injects SO_2 into the last chamber or a special chamber placed between this and the Gay-Lussac tower (Ger. P. 88368). The mixture of gases in this case should be very thorough, and he therefore prefers to employ the SO_2 not as burner-gas, but in the shape of a large quantity of gas from the first chamber, where much SO_2 is still present (Ger. P. 91260). This last idea is evidently much the same as the various proposals formerly made for mixing the chamber-gases from various parts of the system (*suprà*, pp. 648 *et seq.*).

The success of the working of the Gay-Lussac towers depends also upon the proper *regulation of the draught.* If the draught is insufficient, the chamber-process will from the outset be injured by the continual leakage of gas and by all the other drawbacks already enumerated, and specially by the behaviour of the pyrites in burning. In that case the Gay-Lussac tower itself will not work properly; for unless a sufficient excess of oxygen be present in the last chamber before the gas leaves it, unoxidised nitric oxide will remain behind, which passes through the tower unabsorbed and only forms red vapours when issuing into the outer air. At the same time there will be sulphur dioxide present in this case; and this acts still worse, since it decomposes the nitrososulphuric acid still present in the vitriol with which the coke in the tower is soaked, and carries away its nitre as nitric oxide. If the waste gas, as previously insisted upon, contains 5 or 6 per cent. of free oxygen, the above cannot happen to an appreciable extent.

If, on the other hand, the draught is too strong, and therefore the kiln-gas is too poor, the sulphur dioxide will not have time to condense within the chambers as sulphuric acid; it will partly get into the tower, and there cause the decomposition just mentioned and a loss of nitrous compounds.

In both cases, therefore, the same result will happen as if the last chamber did not contain an excess of nitre-gas; and if nitre is too much economised, it will indeed be wasted all the more in the way just described, the sulphurous acid driving off the nitrogen of the tower-acid into the air in the shape of nitric oxide.

Such a *faulty working* of the tower will reveal itself by the escape of a large quantity of red vapours out of the chimney, by the tests of the tower-acid, and even by its appearance, since the acid, which otherwise is nearly or quite colourless, turns a dark purple colour, and is filled with countless small bubbles of nitric oxide, at the same time getting heated by the formation of sulphuric acid (Bode, in a note to the translation of H. A. Smith's pamphlet, p. 122). It is therefore the worst case of all, if alternately sulphur dioxide gets into the tower and the reverse. In that case nitrous vitriol is alternately produced and again decomposed. When, however, sulphur dioxide constantly passes into the tower, there is no absorption of nitre-gas at all, and the tower in this case does not act as an absorbing-apparatus, but simply as a continuation of the chamber-space (Bode, *ibid.*, p. 124). This proves, as Bode justly remarks, that one improvement, viz., the recovery of the nitrous acid, necessarily led to another, viz., to a better condensation of the sulphur dioxide, or a better yield on the sulphur burnt.

The loss of nitre caused by this imperfect action has been often underestimated, especially formerly when the methods for testing the exits were defective; indeed the very reasons which impede the full action of the Gay-Lussac tower will cause similar losses during the bubbling of the exit-gases for the purpose of testing through the absorbing-liquids on the small scale. It is quite certain that the loss of nitre in the exit-gases indicated by Jurisch and others is far below the truth, and that this vitiates by itself most of the reasoning concerning the "chemical loss" in the Glover tower. Benker (quoted by Sorel in his *Traité*, p. 313) has found that the Gay-Lussac sometimes allows two-thirds of the nitrous gases to escape, and Sorel (*ibid.*, pp. 313 and 393) agrees with him, on the strength of calculations founded upon the vapour-tension of N_2O_3 in nitrous vitriol. He found this *unavoidable* loss to cover very nearly the whole loss of nitre in his chamber system, viz. 2·66 per cent. out of 2·8 per cent. $NaNO_3$ for 100 S, leaving practically no "chemical loss," since that a little nitre escapes with the sulphuric acid withdrawn for use or sale.

Petersen (Amer. P. 904147; Ger. P. 208828) claims to avoid disturbances in the "intense working" of the chambers (*cf.* pp. 639 *et seq.*) by placing a column, fed with cold nitrous vitriol of 55° Bé., as "regulator" between the last chamber and the Gay-Lussac tower. Any SO_2 escaping from the last chamber is oxidised here, and the nitrous vapours formed thereby are retained in the Gay-Lussac. If, on the contrary, the gases leaving the last chamber contain an excess of nitrous acid, this is retained in the regulator, thus lessening the work of the Gay-Lussac tower. He replies to an attack made upon his system by Nemes (*Z. angew. Chem.*, 1911, p. 387) in the same Journal (1911, p. 1811). According to the *British Alkali Inspectors' Report* for 1909 several factories had obtained satisfactory results by the introduction of Petersen's "regulator" in respect of cooling the gases and completely utilising the SO_2. Petersen later on (Ger. P. 225197), in order to economise Glover tower space, recommends denitrating the nitrous vitriol, formed in the regulator and in the principal Gay-Lussac tower, in one and the same Glover tower. In this case the regulator is fed with chamber-acid. His Ger. P. 226793 states that the sulphuric acid in the Gay-Lussac towers is most fully utilised by converting the ferrous sulphate contained in the acid into ferric sulphate, before employing it for retaining the last portions of the nitrogen oxides.

The *exit-gases issuing from the Gay-Lussac towers*, even when these are of very large dimensions, are never free from either sulphur or nitrogen acids, and must be regularly tested to comply with the demands made by law, as will be described later on.

We cannot indeed expect the Gay-Lussac tower to absolutely retain the last traces of acids, especially the nitrous fumes, for the following reasons: that a solution of N_2O_3 or of HSO_5N in sulphuric acid of 140° Tw. possesses already a certain vapour-tension, causing some N_2O_3 to be volatilised in a current of air (*cf.* p. 346); that the contact of the gases with the acid can never be made absolutely perfect; and that the time during which this contact takes place is very short. Sorel (*loc. cit.*, p. 313) calculates it for the best and largest apparatus at two minutes as a maximum.

It is a well-known fact that at the very best-managed acid-works the gas issuing from the Gay-Lussac tower has a slight ruddy or orange colour, most of which is probably caused by NO, which finds too little oxygen within the tower, but turns into NO_2 in contact with air. Most acid-makers regard it, from experience, as a bad sign for the working of the chambers, if the orange vapours entirely cease. The Benker process (p. 839), which has a tendency to increase the quantity of NO, must also increase this orange vapour in the exit-gases, which, of course, is best noticed where the gases issue from the Gay-Lussac straight into the air, not into a chimney.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 303) gives a table of averages of the amount of acids contained in the gases both on entering and on leaving the Gay-Lussac tower. The gases on entering contain from 3 to 4 gr. of acid per cubic foot, reckoned as SO_3 (but in reality consisting of sulphur dioxide, sulphuric acid, in the shape of mist and nitrogen acids), on leaving only about 1 or 2 gr. He believes that, if the gases contain more than this quantity, it indicates that sulphur dioxide has penetrated into the absorbing-tower, the result being a reduction of nitrous acid and loss of nitre. On principle this is, of course, correct, but it is not certain whether the above amount is the real limit in all ordinary cases. Crowder also noticed that the proportion of oxygen in the gases issuing from the tower is always slightly larger (0·08 to 0·54 per cent.) than that passing in. The explanation of this phenomenon proposed by him, viz., the diminution of volume consequent upon the removal of SO_2 or some decomposition of the oxides of nitrogen, is altogether inadmissible; any chemical action of the SO_2 and the nitrogen oxides within the Gay-Lussac tower could only tend to diminish, not to increase, the amount of oxygen, and the shrinkage caused by the removal of those gases is far too slight to be observed in gas-analysis (it is, of course, useless to expect such gas-tests to give accurate results, even in the first decimal per cent.). I have little doubt that Crowder's observation was due to some air being drawn into the exit-tube by a slight leak or by the feeding-holes sucking in a little air; this is extremely probable, as the Gay-Lussac tower offers a very great resistance to the draught, and the inward suction at the exit-tube, as shown by an air-gauge, is consequently many times greater than that at the inlet-tube.

Attempts have been made, but hitherto entirely in vain, to absorb or utilise the last traces of acids in the exit-gases. Sometimes they are washed with water in a small coke-tower or plate-column, but this does not do much good.

Mitarnowski and Benker (Fr. P. 210989) propose passing these gases through a solution of ferric sulphate, or through a column charged with granulated copper and fed with water, in order to produce sulphate of copper; but this will hardly pay, for the same reason as that which is at the bottom of the necessarily incomplete action of the Gay-Lussac tower.

A proposal made by Frémy to absorb the SO_2 in the exit-gases from the Gay-Lussac tower by a coke tower fed with nitric acid is characterised by Sorel himself, who reports it (*Traité*, p. 314), as an absurdity, and an idea never likely to be carried out in practice, since there is trouble enough to keep back the nitrous vapours without creating them anew at the last. Frémy's designation "tour aéronitrique" is the only fine thing about this proposal.

Taraud and Truchot (Fr. P. 425913) wash the chamber exit-gases in one or two towers by water (introducing air or oxygen if necessary), and return the weak sulphuric acid formed to the chambers as a spray. Then follows an alkaline washing; the liquids formed here are also returned to the chambers (B. P. 9461, of 1910).

The same inventors (Fr. P. 431427) wash the gases leaving the Gay-Lussac tower by an acid solution of a ferrous salt, decompose the compounds of NO with ferrous sulphate formed thereby by heating the solution, and reintroduce the NO into the chambers.

Various Plans for Recovering the Nitre in Other Ways.

Merely for the sake of completeness it may be mentioned that several other plans have been proposed for utilising the nitre-gas escaping from the chambers. Not one of these has ever possessed any practical value; and they can hardly be said to have even an historical interest, since they have never been employed except in a few isolated cases.

Kuhlmann, for instance, employed thirty Woulfe's bottles, the first ten of which were filled with water, the second ten with a solution of barium nitrate, and the third ten with barium carbonate suspended in water; the mixture resulting in the last ten bottles was used in the second ten bottles, where barium sulphate ("permanent white" or "blanc fixe") was precipitated. Others have used milk of lime, ammoniacal liquor, or even pure water for the absorption of the acid vapours. All these plans are so very much less advantageous or complete than Gay-Lussac's process that they cannot at all compete with it.

G. Wachtel (*Dingl. polyt. J.*, ccxlv. p. 517) proposed forcing the exit-gases by means of a Körting's injector through a red-hot iron or fireclay retort filled with iron-turnings. Here the nitre-gas is to be reduced to ammonia, which is to be absorbed by hydrochloric or sulphuric acid. Nobody seems to have been rash enough to make a practical trial of this plan.

Guye (Fr. P. 404630) recovers the oxides of nitrogen, pure or mixed with other gases, by causing them to react with other liquids in such manner that they dissolve therein, converting these oxides into nitrogen peroxide by treating them with oxygen, or into nitrous acid by treating them with NO.

DENITRATION OF THE NITROUS VITRIOL.

The operation going on in the Gay-Lussac towers whose final result is the production of an acid more or less charged with nitrous compounds, viz. the "nitrous vitriol," requires as its necessary complement another operation, by which the nitrous vitriol, which by itself has no practical use, can be reintroduced into the chamber-process, both in order that the absorbed nitrous compounds may be restored, and that the sulphuric acid originally employed may be recovered in a pure state. It cannot be denied that Gay-Lussac was not sufficiently successful in completing his invention (which has proved so important and useful in the manufacture of sulphuric acid) in this particular; and it is more than probable that the slow extension of his process, nay, even the far from exceptional abandonment of it where it had been introduced in the first instance, must be attributed to the fact that the denitration of the nitrous vitriol was attended with too many difficulties, expenses, and breakdowns of apparatus. The invention of the *Glover tower*, which does away with all this, must therefore be regarded as almost equally important as that of the Gay-Lussac tower itself; and in fact the *general* introduction of the latter only dates from the time when manufacturers were able to combine it with the Glover tower.

The various contrivances for denitrating nitrous vitriol were described and criticised thoroughly and in detail by Fr. Bode, in 1876, in a paper *On the Glover Tower*, which obtained the great prize of the Berlin Society for the Promotion of Industry; and this essay has been used to a great extent in the following description. Bode's paper has also been published by instalments in *Dingl. polyt. J.*, vols. ccxxiii. to ccxxv.

The methods for denitrating nitrous vitriol are founded, on the one hand, on diluting it either with hot water or steam, or with a combination of both; and, on the other hand, on the action of sulphur dioxide, mostly combined with a certain amount of dilution. That in these cases the nitrososulphuric acid is completely decomposed, either by the dilution or the action of the sulphuric acid, has been proved in detail by theoretical investigations. We shall now treat of the apparatus and modes of procedure employed in practice for that purpose.

Denitration by Steam or Hot Water.

One of the oldest apparatus for denitration by steam was described in Payen's *Chimie Industrielle*, and has been copied from this into most text-books; it may be called the "shelf-apparatus."

It is shown in Fig. 302 and is easily understood: F tank for nitrous vitriol, *e* outlet-tap, *d* inlet-pipe, *a a* shelves with overflow-edge, *l*, which retains a 4-in. layer of acid on each shelf, C inlet for burner-gas, *b* steam-pipe, *c* outlet for denitrated acid into the lead chamber D, E outlet for nitrous fumes into the same.

Another apparatus, constructed on the same principle as that just described, is the "Dénitrificateur" proposed by Gay-Lussac himself. It is a lead column of square or circular section, provided with a grating a little above the bottom, and packed with coke on the top of this. The nitrous acid runs in at the top, and is scattered by means of a rose. Below the grating the gas of the sulphur- or pyrites-burners enters and meets the nitrous vitriol descending; at the same time either a jet of steam is introduced separately, or the gas is previously conducted through tanks filled with water, in order to be saturated with moisture.

In these apparatus the denitration evidently takes place by the joint action of the steam and the sulphur dioxide. The acid ought to arrive at the bottom entirely free from nitrogen compounds; but it is then so dilute that it must be run back into the chambers. Such apparatus are not to be found in use in any place at the present day, for good reasons. Since the acid is in them diluted to the same extent as in the process of denitrating by hot water or steam alone, they present no advantage over the latter; indeed they were in the first instance replaced by the latter processes. But the apparatus just described have this drawback, that they last a very short time, on account of the rapid destruction of the lead. The destructive action is always very strong in the first chambers, which, even under the best conditions, and in the presence of a Glover tower, suffer more than the remaining chambers, and have to be made of thicker lead if they are to last as long. This is due partly to the heat of the gas, partly to the nitrous compounds themselves. It is evident that much more of this action must take place in a very small chamber, such as the "shelf-apparatus" or Gay-Lussac's "Dénitrificateur." The worst, however, of these apparatus is that the steam introduced

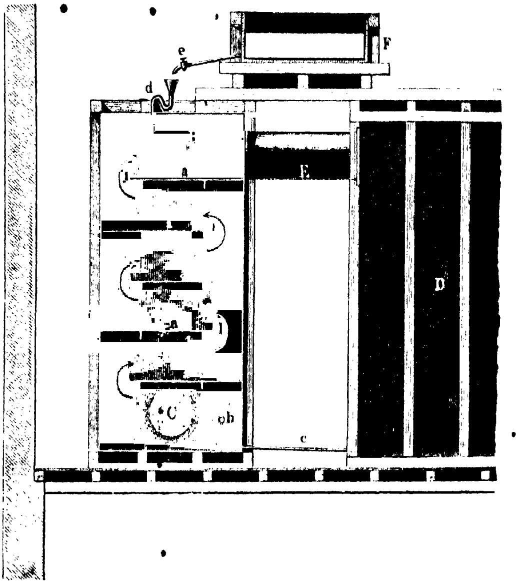


Fig. 302.

into them necessarily leads to the condensation of very dilute sulphuric acid and nitric acid on the sides of the apparatus, which must rapidly corrode the lead. Moreover, considering the small size of the chambers serving as shelf-apparatus or dénitrificateurs, any changes in the chamber-process, in the composition of the kiln-gas, of the supply of steam, of the outer temperature, etc., must be felt in them very much more than in a large lead chamber. Therefore, from time to time, stronger nitrous vitriol will condense on the walls, and be diluted directly after by an increased condensation of water, and thus become charged with nitric acid. The inside of the walls of a working lead chamber is always covered with a white slimy lining of lead sulphate, which retains acid like a sponge, but at the same time protects the lead from further action, until such time as the acid is diluted by condensed steam, gas is given off from it, and the slimy mass of lead sulphate is loosened and washed off, whereupon the lead is again exposed to fresh attacks. The older denitrating-apparatus, therefore, were exposed to very rapid destruction, because they employed the simultaneous action of sulphur dioxide and of steam, and were therefore soon abandoned.

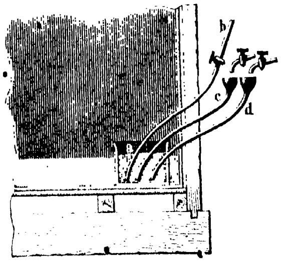


FIG. 303.

In England, most manufacturers passed over to *diluting the nitrous vitriol* in separate small *boxes with water and steam*, whilst on the Continent usually "steam-columns" or "cascades" were preferred. The English arrangement, such as was almost general in former years, but has been placed in the background by the Glover tower, is shown in Fig. 303. *a* is a lead vessel, about 1 ft. high and 18 in. wide, which stands within the lead chamber, very near the inlet for the kiln-gases. Three pipes, *b*, *c*, and *d*, lead into *a*, passing through the side of the chamber and burnt into it. Of these *b* conveys steam, *c* water, and *d* nitrous vitriol; *c* and *d* end in funnels, through which the liquids run. The steam comes from a steam-boiler. The vessel *a* is first filled with water; this is then heated to the boiling-point by steam; and now steam, water, and nitrous vitriol are admitted in such proportions that the latter is completely denitrated before it can run over out of the box *a*. The proximity of the gas coming from the pyrites-burners acts in this way: the escaping oxides of nitrogen are at once spread through the chamber and are mixed with the other gases; and at the same time the gas protects the lead against corrosion.

More perfect is the arrangement formerly usual on the Continent, where the denitration takes place on *cascades*, exactly similar to those described previously (p. 712), only with the addition of a contrivance for introducing hot water.

The *denitration by steam alone*, or by steam with very little water, takes place in the so-called *steam-column*, which is shown in Fig. 304 on a scale of 1 : 25, as it was worked at Freiberg some time ago. It consists of a cylinder of strong sheet-lead 11 ft. 6 in. high, 3 ft. wide, composed of three drums, joined at *a* and *b*, and strengthened by hoops. It is lined with acid-proof bricks, B, joined by a mortar made of fireclay and boiled tar [or of asbestos and silicate of soda, *cf.* p. 831]. The bottom is formed by a lead plate A (or better a loose saucer), the top by a stoneware slab C. D is the feed-pipe for acid, E outlet for nitrous vapours, F steam-pipe, whose mouth is covered up and built round with bricks in such a way that proper channels remain for the steam and the acid. On the top of this the column is filled with bits of flint nearly up to its cover; they are about the size of a fist near the bottom, and decrease towards the top to the size of a walnut. In place of these some works use bits of broken stoneware. The nitrous vitriol running in at the top trickles down through the bits of flint, and is decomposed in this way by the rising steam. Whilst the nitrous acid given off from it goes away into the chamber through the pipe E in the state of vapour, the sulphuric acid, diluted by the condensed water, arrives at the bottom of the steam-column, and runs through the pipe G into the tank H. The pipe G is so bent as to remain always luted by the acid.

According to Bode, such a column, at Freiberg, sufficed for a system producing 126 cwt. of sulphuric acid of 170° Tw. in twenty-four hours.

In a large factory near Newcastle there existed, till 1873,

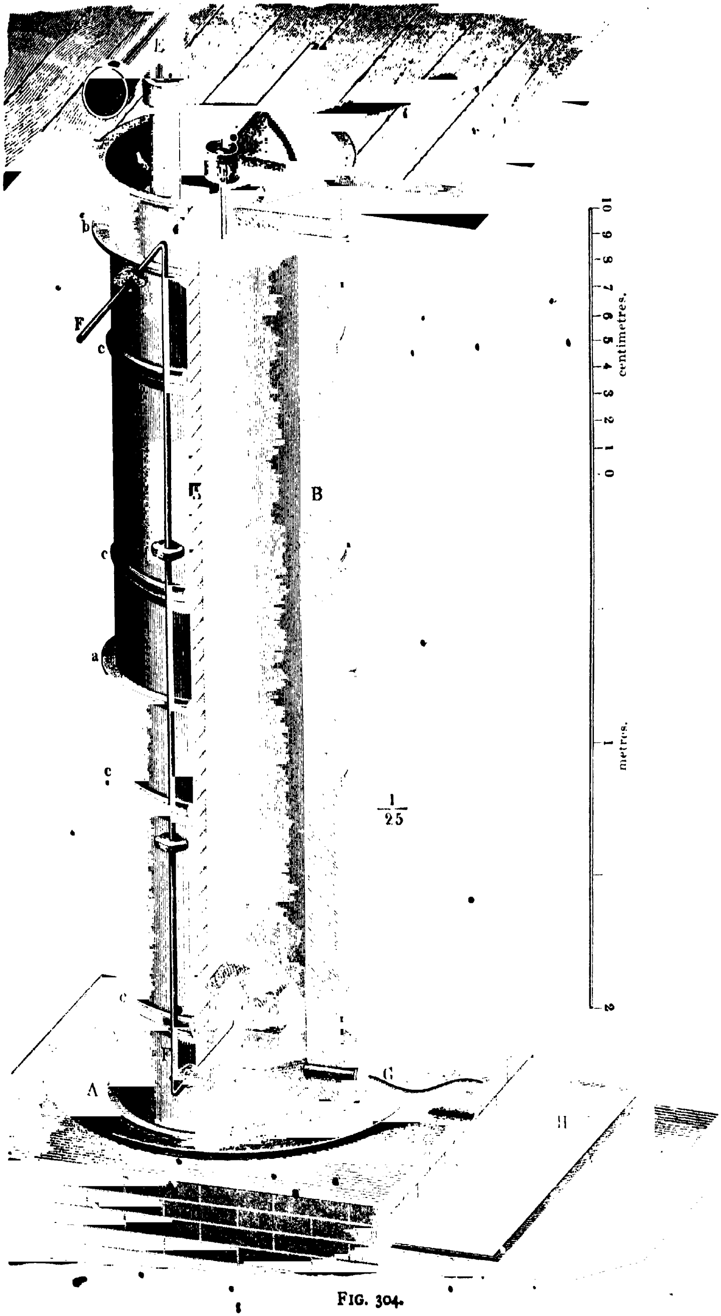


FIG. 304.

steam-columns consisting of a cast-metal pipe 3 ft. wide and 9 ft. high, with a lining of lead and another lining, inside the first, of thin bricks (2 in.), and a packing of flints. Since then they have been replaced by a Glover tower.

There are also steam-columns made without a lead jacket; but they cannot in this case be built up of bricks, but must be made in one or two pieces. Bode shows such a column, erected by Dr Gilbert at Hamburg (Fig. 305). Its inner diameter is 1 ft. 3½ in., its height 13 ft. 1 in. It consists of two gas-retorts, *a a*, made tight at the joint, after heating the same, by asphalt. The bottom, *b*, and the cover, *c*, are formed of round fireclay-slabs; the latter contains an opening for the stoneware pipe *d* for carrying off the nitre-gas and the excess of steam into the chamber. The nitrous vitriol enters at *e*, the steam at *f*, and the denitrated sulphuric acid runs off at *g*. The retorts are surrounded by the cylinders *h h*, of ½-in. cast iron, which are bolted together and to the cast-iron top and bottom plates. A space of 1½ in. remains between the cast iron and fireclay, and is filled with melted asphalt having a very high fusing-point. The column is filled with bits of flint; the mouth of the steam-pipe is protected by loose bricks. This apparatus in Bode's time had been in operation for five years without giving any trouble, and supplied a set of chambers making 6 tons of acid of 170° Tw. in twenty-four hours.

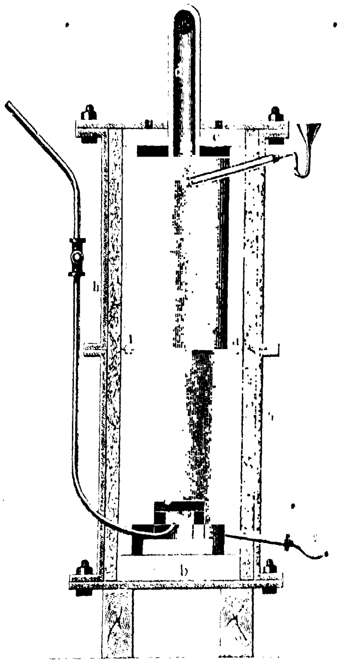


FIG. 305.

In other works the steam-columns are made much smaller, which is evidently quite sufficient. In Würtz's *Dictionary of Chemistry*, iii. p. 157, Scheurer-Kestner figures a column made of a piece of Volvic lava 6 ft. 6 in. high, and only 8 in. wide inside, 3 ft. outside, filled with broken glass. The whole is surrounded by a lead casing. Such a column suffices for a chamber of 4000 cb.m., turning out 8 tons O.V. per day. These Volvic columns seem to stand better than any other kind of steam-column, but they also crack sometimes.

As late as 1890 I found in Hamburg a steam-column of the following construction. It consisted of a cast-iron cylinder, lined with bricks inside; the bottom part, about 8 in., was made of lead and dipped into a very thick cast-lead dish, forming a hydraulic lute, just at the point where the steam entered. The outflowing acid was kept at 112° Tw.; it tested on an average 0·05 per cent. N_2O_3 and 0·01 per cent. NO_3H, which seems very good work for that strength.

Bode asserts that the simplest and cheapest apparatus of this kind consists of ordinary stoneware receivers, as shown and described, pp. 567 to 569 of our second edition. This kind of denitrating-apparatus does not appear to be in existence anywhere now; probably it would stand but a very short time. We also refer to the same place for Bode's comparison of the efficiency of steam-columns, of cascades and stoneware receivers, as being devoid of actual interest at the present time.

In 1902, steam-columns were still used at Freiberg for denitrating nitrous vitriol. The reason for retaining these apparatus was that the gases at those works enter the chambers at the temperature of the surrounding air, and it was assumed that this is too low for working a Glover tower; but it is doubtful whether this assumption is correct (see later on).

Evers (Ger. P. 182216) employs denitrating towers especially adapted to spent nitrating mixtures of explosives factories, not packed completely from bottom to top, but separated by perforated partitions into chambers, which increase in size from the bottom to the top, and are in turn filled with packing or left empty, the latter being fitted with a mixing-apparatus. The denitrating mixture of air and steam is previously heated to at least 400°. The acid to be denitrated passes downwards from one chamber to another. This plan is highly recommended by

Rudeloff (*Z. Schiess- und Sprengwesen*, 1907, p. 144) from his own experience, but is sharply criticised by Guttmann (*ibid.*, p. 217). Rudeloff (*ibid.*, p. 257) replies to this, upholding his former statements, and adding that Evers' denitrating-apparatus is employed in a dozen German explosives factories. The highest loss of nitric acid is 0·24 per cent., of sulphuric acid 0·03 per cent. Four-fifths of the nitric acid comes out as 40° Bé., one-fifth 36° Bé., with at most 0·3 per cent. N_2O_4 and traces of H_2SO_4. The sulphuric acid is 60° Bé., clear like water and free of HNO_3. Coals for denitrating 1 ton of mixed acid, 30 kg., and 18 kg. coke for heating the air. One apparatus denitrates 10 tons acid in twelve hours, and is attended to by one workman.

Glover Towers.

The apparatus which is now used for denitration in nearly all vitriol works is the *Glover tower*, which is properly treated in this chapter, since its inventor had in the first instance constructed it for denitration, although it might just as well be described as a cooling and a concentrating apparatus. The Glover tower was invented by the late Mr John Glover, of Wallsend, near Newcastle-on-Tyne. According to personal information received by myself from Mr Glover, he had already built his first tower in 1859, at the Washington Chemical Works, near Durham. This tower was made of fire-bricks and packed with a network of thin fire-tiles. It lasted a year and a half, and proved the correctness of the principle. In 1861 Glover, at the same place, built a lead tower; and when erecting another works at Wallsend in the same year, he, of course, built a similar tower there as well, which worked until 1863 or 1864. From the experience gained in this way, Glover constructed in 1864 a third tower, which in all essential respects was the same as is used to this day. Up to that time only his nearest neighbours had introduced the tower. It must here be observed that its inventor had not only taken out no patent for it, but, with great liberality, had shown it to every one interested in the matter. In spite of this, some of the manufacturers on the Tyne, intending to "improve" the tower, committed mistakes in its construction; and, at least in one case, this led to its being given up again, although it has since been reintroduced. Between 1868 and 1870 all the larger and better-managed works on the Tyne introduced the Glover tower; it was adopted in Lancashire about 1868, in London in 1870. Until 1871 nothing had been published about the Glover tower; and it was entirely unknown outside a limited number of English alkali-works till I published a paper on it in *Dingl. polyt. J.*, vol. cci. p. 341, which made it generally known, and led to its adoption, first in Germany, then elsewhere. Soon after my publication objections were raised against the tower as a denitrating apparatus (nobody has ever doubted its excellence as a concentrating and cooling apparatus). The first objections raised by Bode (*Dingl. polyt. J.*, ccii. p. 448) were immediately refuted by me (*ibid.*, p. 532), and have since been withdrawn by Bode himself. Bode has become one of the most zealous constructors and advocates of the Glover tower. Also the objections raised by M'Culloch (*Chem. News*, xxvii. p. 135) have been answered by Glover (*ibid.*, p. 152), by me (*ibid.*, p. 162), and Bode (Prize Essay, p. 5). M'Culloch himself afterwards changed his opinion. Much more serious objections were made by Kuhlmann (*Hoffmann's Official Report on the London Exhibition of* 1862, p. 174) and by Vorster (*Dingl. polyt. J.*, ccxiii. p. 506), on the assumption that the contact of hot sulphur dioxide and nitrous vitriol in the tower must cause a considerable loss of nitre compounds in the shape of nitrous oxide or of free nitrogen. It is certainly a fact that, under certain conditions, hot sulphur dioxide reduces the nitrogen oxides down to nitrogen protoxide or even to nitrogen. But that such conditions exist in the Glover tower Kuhlmann could not prove, because he had no such tower at his disposal; nor did Vorster experiment with the tower itself in this direction, although he made other interesting observations respecting it; but, entirely on the strength of laboratory experiments, he asserted that 40 to 70 per cent. of the nitrous compounds were lost in the Glover tower. His experiments, however, were made under totally different conditions from those existing in the Glover tower; and I succeeded in refuting Vorster's inferences on the loss of nitre from his own figures (*Dingl. polyt. J.*, ccxv. p. 56, ccxvi. p. 79). In the experiment considered by Vorster as the most conclusive, he passed hot sulphur dioxide mixed with air for twenty-seven minutes through nitrous vitriol heated to 180° C.;

and it is inconceivable how he could assert that this condition answers to that in the Glover tower. Into this the nitrous vitriol enters quite cold, mixed with chamber-acid; and only on leaving, when its heat is greatest, does it attain 130° C. It is out of the question that it should have that temperature in any considerable part of the tower, much less 180°, as in Vorster's experiment. On the contrary, that acid which shows a rather elevated temperature (but never anything like so high as in Vorster's experiments) contains next to no nitrous acid, but is only further concentrated by hot kiln-gas; and, at all events, the denitration takes place to the greatest extent in the upper part of the tower, where the acid is still pretty cold. This follows with certainty from the well-known fact that the denitration of dilute acid takes place readily, that of concentrated acid with great difficulty. Apart from this, the acid is never exposed to the current of hot sulphur dioxide such a long time as in Vorster's experiments. If once the packing has been quite impregnated, the acid gets from the top to the bottom in a few minutes; but owing to its fine division, it is almost entirely denitrated near the top. In short, Vorster's experiments are useless for deciding the matter in question, even if they were not refuted by the plain fact, that with the Glover tower the waste of nitre is *at least* no greater than with any other process. This subject is noticed more fully below.

Subsequently (*Ber.*, x. p. 1432—more explicitly in *Dingl. polyt. J.*, 1877, ccxxv. p. 474) I criticised in detail the experiments and statements of Kuhlmann and Vorster, and proved their irrelevancy. I further proved by experiments that if the sulphur dioxide is mixed with a similar excess of oxygen as in the kiln-gas, this mixture decomposes nitrous vitriol, even at a temperature of 200° (in the Glover tower it never gets beyond 130°), in such a way that the *whole* of the nitrogen oxides can be recovered by absorption in concentrated sulphuric acid. Pure sulphur dioxide, free from oxygen, does not act on nitrous vitriol at 110° to 130°, but only at 200° C., in such a way as to cause the formation of some nitrous oxide. This, however, is not a practical case at all; and it is certain that in the Glover tower neither nitrogen protoxide nor nitrogen is formed in appreciable quantities. My experiments and calculations were attacked as inaccurate by Hurter (*Dingl. polyt. J.*, ccxxvii.

pp. 465 and 563), but were completely vindicated by me (*ibid.*, ccxxviii. pp. 70 and 152).

If there were any truth whatever in Kuhlmann's and Vorster's assertions, it would certainly be a cause of still greater loss when the fresh supply of nitre-gas is carried through the tower, as is done in the great majority of English factories, or when even the liquid nitric acid is run through it, as in most continental works. Then not merely 70 per cent. of the nitrous vitriol, but also 70 per cent. of the fresh supply of nitre, or nitric acid, would be wasted by the tower. This certainly would be felt very badly indeed. But already in 1871, of the ten works on the river Tyne which possessed Glover towers, only three worked so as to decompose the nitre by the gas of separate pyrites-burners, and to take the gaseous mixture past the Glover tower direct into the chambers. The other seven works sent the gas of *all* burners, together with all the fresh nitre-gas, through the tower, *without consuming any more nitre* than the three former ones. Among these three works was that managed by myself, and in my first publication I recommended this arrangement. Later on, from experience gained in the meantime, the plant was altered, and *all* the kiln-gas, together with the nitre-gas, was taken into the Glover tower; but no extra consumption of nitre whatever could be detected. In the same way Mr Schaffner, of Aussig, found no extra consumption ensue when he began introducing all the liquid nitric acid through the Glover tower. Cf. *suprà*, p. 713.

It is absolutely certain, from the practical experience of many works, that with the Glover tower rather less nitre (never more) is used than with steam-columns or cascades. This is corroborated, for instance, by the former opponent of the Glover tower, Bode, in *Dingl. polyt. J.*, ccxvii. p. 305, and in his Prize Essay, p. 87; and, altogether, no contrary statements of those who have had practical experience of the tower have been made known. On the contrary, the Glover tower has not only been generally accepted in England, but also on the Continent. Already in 1875 the Berlin Society for the Promotion of Industry offered a prize for an essay on this subject, in which the utility of the Glover tower for most cases is expressly presupposed, and only its applicability for kiln-gas of inferior heat is mentioned as doubtful and requiring examination. The result of this was Bode's often-mentioned essay on the Glover tower. At the present day the Glover tower forms an essential part of every well-arranged sulphuric-acid works, and ranks with the Gay-Lussac tower. Certainly it will not answer to expectations when constructed in an improper way or with unsuitable material, and therefore, at first, its use was here and there discontinued; but the same may be said of every apparatus used in the whole range of industry; and the *consensus* of the great majority of manufacturers has entirely decided *for* the Glover tower. Bräuning (*Z. J. Bergwesen*, etc., 1877, p. 140) also quotes the experience of a whole series of works at Oker in which the tower was employed, and where, since its introduction, less nitre was used than before, in consequence of the acid being completely denitrated, so that no loss can be incurred through the reduction of nitric acid to nitrogen or nitrous oxide. During my extensive tours through a number of the best English, German, and French alkali-works, I have everywhere received the same information, viz. that since the introduction of the Glover tower less acid is consumed than formerly (with the diluting process). This may very frequently be in consequence of the chamber-acid being also denitrated in the Glover tower; but in some works the acid of the large (or first) chamber is not kept nitrous at all, and in others, from various causes, only a small portion of the chamber-acid passes through the Glover tower. In no case is there the slightest reason for asserting that the Glover tower, by itself, wastes more nitre than the diluting process. At Malétra's works at Rouen, before the introduction of the Glover tower, 2 parts, since then only 1·3 part of nitre has been used to 100 parts of pyrites.

Hurter himself, in 1877, when he still imagined that a considerable portion of the nitrous gases was reduced to N_2O and elementary N in the Glover tower, admitted that "with careful work" there was no more nitre used after the introduction of the Glover tower than before, as quoted by Jurisch (*Schwefelsäurefabrikation*, p. 153), whose continued adhesion to the long exploded belief in such a destructive action of the Glover tower has been already mentioned in the 6th Chapter, p. 714, and which is probably the last survival of that error. It should be noticed that Hurter, in his many years' position as chief chemist of the United Alkali Company, has never made any attempt at doing away with the Glover towers, formerly condemned by him as destroyers of nitre.

Gay-Lussac himself had at first denitrated the nitrous vitriol by burner-gas *and steam* (p. 846); much later again Cl. Winkler, in 1867 (*Untersuchungen*, etc., p. 24), proposed very clearly the denitration of nitrous vitriol by sulphur dioxide, without being aware of the fact that this plan had been carried out for some years in practice by Glover and others. But these attempts were vitiated by the proposal to add steam or water, and they did not embrace the concentrating action of the apparatus which is now called the Glover tower.

Functions of the Glover Tower.—Although outwardly resembling a Gay-Lussac tower, the function of the Glover tower is exactly the opposite—viz., to deprive the nitrous vitriol running off *at the bottom* of the Gay-Lussac tower of its nitrous compounds, and to restore it to a proper state of concentration for applying it again *at the top* of that tower. This, certainly, is only one of the functions of the Glover tower, but the most important and characteristic of all. The tower fulfils this function by exposing the nitrous vitriol, usually mixed with chamber-acid, in a finely divided form, to the action of the hot burner-gas, whose heat acts concentratingly upon the sulphuric acid, and whose sulphur dioxide acts denitratingly upon the nitrososulphuric acid; and the simultaneous concentration and action of the sulphur dioxide seem very much to advance the denitration, which takes place according to the equation:

$$2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

Glover's apparatus cannot be put in the same line with the apparatus described above (pp. 846 *et seq.*), because in it no condensation of dilute sulphuric acid containing nitric acid can take place on the lead walls, and because it is altogether so constructed that the lead nowhere comes into contact with the hot gas and the nitrous vitriol. Once properly built, it continues working for many years, and causes no interruption of the process. Besides, it possesses two very great advantages. The first is, that it is both the most complete and the most rational of all cooling contrivances for the burner-gas: the most complete, because the gas is brought into immediate contact with the cooling-liquid in the shape of a fine spray, not separated from it by a metallic wall or only exposed to the cooling-action at the circumference of the current; the most rational, because no expense has to be incurred for pumping up cold water for cooling, but the generated steam is at once usefully employed in the chamber. The second and still greater advantage of the Glover tower is that in it not only all the acid serving for absorption in the Gay-Lussac tower, but the whole of the chamber-acid is brought to 144° or even up to 152° Tw. without any expense except that of pumping the acid to the top of the tower—an expense which is very small indeed, especially in the case mentioned on p. 723, where the exhaust-steam of the air-pumping engine is used as steam for the chambers.

The Glover tower is, moreover, now mostly used for introducing the requisite fresh nitric acid into the chambers without any special apparatus, by running it down together with the nitrous vitriol. Before it arrives at the bottom it is fully denitrated, as well as the nitrous vitriol itself (*cf.* Chapter V. p. 714).

Even a solution of nitrate of soda has been employed in a similar way, but this has been given up as impracticable (p. 719).

Construction of a Glover Tower.

The constructive principle of the Glover tower is this: to provide an apparatus perfectly tight against liquids and gases, and at the same time capable of resisting both heat and the action of strong acids in the liquid and gaseous form. A gas-tight apparatus is always preferably made of some metal, and this principle is followed in the construction of vitriol-chambers. But lead, the only metal to be thought of, does not resist the action of hot acid-gases at temperatures not very far removed from its melting-point. Acid-proof material of any other kind requires making joints with some mortar or cement, none of which again is sufficiently resisting in this case. The solution of the difficulty is attained in this way:—An outer shell of lead constructed as usual in the case of chambers, towers, and the like, is provided with an acid-proof stone or brick lining, *without any mortar*. The latter, which would be destroyed directly, is not necessary for the stability of the erection if it is properly designed, nor need the lining be gas-tight, as the small amount of gas which finds its way through the joints is then sufficiently cooled down not to do any harm. Nor can the lining itself, which is always a bad conductor of heat, transmit enough heat to be dangerous to the lead.

We now come to the question as to what *lining* should be employed. Undoubtedly the best material for this purpose is *Volvic lava* (see p. 831), which resists both acids and heat better than any other material so far known. It occurs near Clermont-Ferrand, in the centre of France, and can be had in large blocks which are easily shaped to design, *e.g.*, from Brosson Lafilichat frères, or from A. Moity, both residing at Volvic (Puy-de-Dôme).

Next to this, where Volvic lava is considered too dear or difficult to procure, comes "chemical" brick or stoneware, *i.e.* such as resists the acids and also the heat up to the required extent, but it need not be "fire-brick" proper. None of these bricks last for ever, and they always yield some alumina to the acid, but they may serve for several years.

In Great Britain the "blue bricks" of Mold in Flintshire are usually employed for lining Glover towers. The following is the composition of the best class called "metalline," supplied by the Buckley Brick & Tile Company, according to *Chem. Trade J.*, x. p. 46:—63·01 SiO_2, 25·95 Al_2O_3, 6·49 Fe_2O_3, 0·75 Mn_3O_4, 0·83 CaO, 0·40 MgO, trace of Na_2O, 2·57 K_2O, 0·9 organic substance, and water.

In Germany the bricks made at Bad Nauheim, at Bendorf, near Coburg, and at Aussig are mostly used.

The manufacture of acid-proof bricks for Glover towers, according to *Tonindustrie Zeit.*, 1890, p. 642, requires clay rich in silica more than in alumina, of a dense, non-porous character. Some descriptions of clay which are almost free from iron and can be burned to a clinker can be used directly. Where no such clay is available, an artificial porcelain-like mixture can be made with from 25 to 30 parts felspar, 25 to 30 best china-clay or other good fire-proof clay, and 40 to 50 parts quartz. It should be burnt to a clinker, and should not shrink too much in the process. The bricks are best covered with a glaze consisting of 54 parts quartz, 84 felspar, 35 ground chalk, and 26 ground china-clay.

A special lining for towers (Gay-Lussac, Glover, or intermediate "reaction towers") is described in Skoglund's Amer. P. 640037. It consists of sodium or potassium silicate, mixed with quartz powder and then treated with sulphuric acid, which takes out most of the alkali and leaves a mass not acted upon by acids, and easy to work. It is put on in a layer of ½-in. thickness and dried by fire-heat. The "obsidianite," mentioned in *Chem. Trade J.*, 1909, xliv. p. 181, and 1912, l. 70, is evidently very similar or identical with the above.

Karyscheff (B. P. 2994, of 1907) makes acid-proof bricks from powdered spinels, chromite, ceylonite, and similar minerals by agglomerating them by means of a cement under heavy pressure.

The "packing" of the Glover tower is made of similar material to the lining, but this will be treated later on (p. 867).

We shall now explain the principles of constructing the various parts of a Glover tower.

The *foundation* of a Glover tower can be made of strong brick pillars, with a roof formed by a strong brick arch and braced together with iron stays and rods. The pillars may also be joined by strong railway rails, instead of an arch, and they may be themselves constructed of cast iron, which makes the foundation much lighter and more accessible. The top of the foundation is covered by a lead apron 6 or 7 lb. to the square foot, for the purpose of protecting it against acid drippings. This apron may be turned up so as to form a saucer with an overflow spout; and if this be kept full of water it will help to preserve the inner saucer, by keeping this at a moderate temperature.

Sometimes the platform at the top of the foundation is covered with a molten mixture of pitch and brimstone, and the leaden apron is put upon this while still warm. This is an absolute protection against any corrosion of the iron pillars and girders by any acid finding its way down.

The *frame* of the tower must, of course, be different according to whether the tower is angular or circular in section. The former kind will be made clear by the designs shown later on; the latter is distinctly seen in the section of a French Glover tower, lined with Volvic lava, given below.

The material of the frame is mostly wood, preferably pitch-pine, but iron frames are very appropriate in this case. In both cases the frame has to support the acid-tanks required for feeding the tower, and also the light shed covering the top.

The *tower itself* is made of 14-lb. lead, its bottom of 35-lb. lead, the straps of 9-lb. lead. Its sides are suspended from the top and side joists, just like those of a chamber. The lead stands a little off the wood, which is of importance for the protection of both the wood and the lead. In order to avoid seams at the corners, where they would be weakest and where they could not be very well repaired on account of the frame, two of the sides are made of two sheets of lead (1, 2, Fig. 306) each, which are burnt together in the middle, and which reach round the corners, where the sheets 3 are burnt to them. The seams are best burnt outside. All the side sheets reach down from the top to the bottom without any horizontal seams, and hang loosely within the saucer.

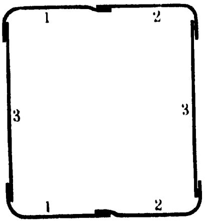


FIG. 306.

Sometimes even square or oblong towers are not made in this way, but are constructed in single drums, like the circular towers (*vide infrà*), the higher one always resting on the bevelled-out edge of the lower. This is especially done where the tower-lead is not fastened to the ordinary frame by straps, but is held together by iron rings or closely touching wooden frames, which offer resistance to the thrust of the lining and packing. Iron hoops, however, have the disadvantage of gradually cutting into the lead, and closely touching wooden frames cause the lead to be wasted much more quickly.

The bottom saucer is formed of two sheets of lead burnt together in the middle and turned up all round to a height of 12 in. Since sheets of 35 lb. to the square foot cannot be burnt together in the usual way, they are joined thus: they are placed close together, after having the edges cut off slantingly and scraped clean (Fig. 307); into the rebate, *a*, thus formed, lead heated a good deal beyond its melting-point is poured: the latter, before solidifying itself, fuses the margins of *a*; and this is further assisted by a red-hot iron, so that the whole unites into a solid mass.

Another method of joining such thick sheets of lead is this: cutting the lead as shown in Fig. 307, then heating the borders with a hot iron, and at once applying the blowpipe so that the lead at this place melts for a certain depth and runs to the bottom of the triangular channel between the two sheets and closes this up, whereupon the whole channel is filled up by heating with the blowpipe both the borders and a thick strip of lead, as usual when burning horizontal lead seams (p. 599).

Sometimes, as we have seen above, the bottom of the tower stands in another saucer, filled with water, which is allowed to get hot, but even in this state forms a protection to the inner saucer against overheating. In other cases there is a constant flow of cold water round the bottom saucer, so that the acid gets cooled to some extent before running away, which is an additional advantage. Another plan for cooling the bottom is that which is shown in the designs below, viz., arranging a network of air-channels in the brickwork underneath the lead bottom.

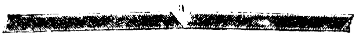


FIG. 307.

Inside the tower bottom is protected by a layer of 3-in. acid-proof slabs; sometimes first a piece of lead is laid loose on the bottom before putting the slabs on.

Lastly, we must notice the "*lip*," where the lead side of the saucer is turned over to form a place for the acid to run off continually into a leaden spout. This part, over which hot acid is incessantly running and which cannot remain covered by a protecting layer of lead sulphate, is exposed to very great wear and tear; and as it cannot well be repaired while the tower is at work, the plumber must not neglect to put a false lip, consisting of a piece of sheet-lead beaten down close upon the real lip. The acid will then run over the false lip; and the latter, when worn out, can be replaced by a fresh piece in a few minutes.

Instead of a "lip," a lead tube of about 1¼ in. bore can be burnt in the side of the saucer, a little below its upper edge; but the plumber must do this with the utmost care, and make the joint extremely strong, in order to save repairs, which can only be made after stopping the work. At Stolberg, where the Glover tower has no saucer, but the bottom and sides are in one piece, two running-off pipes are provided, so that one can serve when the other is stopped up, etc.

The lead top of the tower is suspended from wooden or, better, iron rails, to which it is fastened by straps, and which are supported by the side frame. Towards the centre it is dished out so that any acid leaking from the tanks cannot run down the sides of the tower, but finds its way into the tower through the hydraulic joints of the acid-distributor.

The *inlet and outlet of the gases* require special care. About the outlet-pipe nothing need be said, except that on its bottom a small ledge is formed, which compels the acid squirted into it to run back into the tower; this pipe also usually rises a little towards the chamber. On the other hand, the fixing of the entrance-pipe, which ought to have a slight fall towards the tower, is not quite such a simple matter, and at first caused much difficulty. It is mostly made of cast iron, and has in the great majority of acid-works, except in the above-mentioned cases, a temperature of at least 300° C. The lead of the tower, where it touches the cast iron, will therefore be quickly wasted, and any kind of cement put between the two will not do much good; in most works formerly a little gas was seen escaping at this joint, and it gave occasion for many repairs. The following arrangement obviates this drawback:—The pipe is not at all in contact with the lead, but with a metal casting. The latter is in the shape of a ring with two flanges perpendicular to the plane of the ring; the thickness of the metal is 1 in., the clear space between the flanges 4 in., the total height 8 in., the inner diameter of the ring 2 ft. 9½ in. Since the outside diameter of the inner pipe is 2 ft. 7½ in., there is a caulking-joint of 1 in. left free all round, which can be filled up with any hard cement—for instance, the ordinary rust-cement made of iron filings, sulphur, and sal ammoniac; this cement can be rammed in hard, as it lies between two iron surfaces. In the side of the tower, in the place in question, there is a circular hole to the circumference of which an upstanding flange is burnt, fitting the outer circumference of the cast-iron ring; between the lead and the iron a little ordinary tar and fireclay cement is put; and a wrought-iron hoop in two parts with screw joints firmly binds together lead, cement, and cast iron. Since the outer part of the ring is cooled by the air circulating in the hollow space, only a small part of the heat can be communicated to it, which the inner part of the ring receives (already weakened by the layer of cement) from the inner pipe; and therefore no difficulty is experienced in keeping the joint between lead and iron tight.

At the Aussig works the difficulty is obviated by attaching to the cast-iron gas-pipe coming from the burners a short piece of fireclay pipe with a flange joint; the latter projects into the Glover tower; and the lead side of this is simply joined to the fireclay pipe by a burnt-on flange surrounding the pipe, with tar cement between, and with an iron hoop pressing the lead flange on to the pipe. As the fireclay pipe has much thicker walls, and is a much worse conductor for heat than a cast-iron one, this joint keeps tight even without the air-cooling just described.

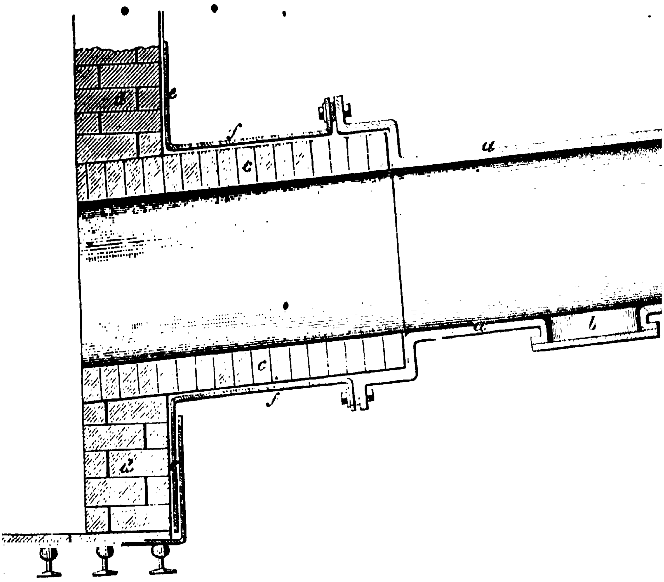


FIG. 308.

The plan followed at Griesheim with perfect success is shown in Fig. 308. The burner-pipe *a a* (which at *b* shows a cleaning-hole at the bottom) is enlarged at its end, so that it embraces one end of the dry-walled annular-shaped brick flue *c c*, whilst the other end is tightly held in the brick lining *d d* of the tower. The lead side of the latter (*e e*) is continued into a lead cylinder (*f f*) surrounding the free portion of the flue *c c*; its end is bent round in the shape of a flange, pressed against a flange of *a a* by means of an iron hoop and screw-bolts; and the joint is made tight by asbestos packing.

At some works the burner-gas is carried into the tower by means of pipes, made of Volvic lava, in two halves, as shown in Fig. 309. In this case no special contrivance is required for protecting the lead at the joint.

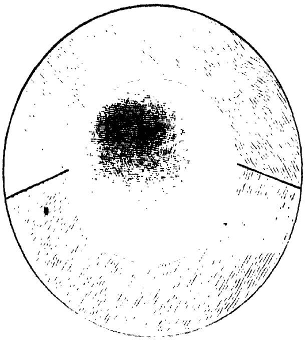


FIG. 309.

Duggan (B. P. 5012, of 1896) employs a water-cooling jacket to the inlet-pipe for the Glover tower.

The *lining* of the tower is made of the materials described above, p. 860, and is so constructed as to serve at the same time as a support for the packing. This is facilitated by the fact that at the bottom, where the hot burner-gas enters, the lining must be anyhow much thicker than higher up, say 2 ft. 3 in. all round. This is continued, say, 4 ft. high, where the thickness of the lining diminishes to 18 in.; the recess thus formed serves, together with a central pillar, for supporting stone slabs which form a grid for the packing. Or else arches are sprung from side to side for the purpose of forming a grid, as shown in the designs below, by being levelled to a plane surface at the top.

Higher up the thickness of the lining decreases to 14 in. and at last to 9 in.

The whole lining of the tower as well as the dome (arch) of the grid must be walled *dry*, without mortar of any kind (p. 859). In order to make the arch sufficiently stable without any mortar, it should not be made of ordinary fire-bricks cut or moulded to shape, but of large fireclay lumps expressly manufactured for the purpose, whose sides join smoothly together. In some works all the bricks of the lining are ground one upon another, so that only extremely small joints remain. This is most easily done where the lining consists only of a few large blocks of Volvic lava (see p. 860, and below).

It is not considered bad work if the lining of a Glover tower stands for three years without having to be renewed; sometimes it stands much longer.

Steuber & Co. (Ger. P. 227283) construct acid-towers without any lead shell, with double sides of acid-proof stones. They protect the foundation against the action of acid penetrating there by means of channels through which fresh water is constantly running (*cf.* also the linings described *suprà*, p. 860).

The *packing* of Glover towers in England usually consists of flints, picked from the chalk and purified by washing with hydrochloric acid. This material is absolutely acid-resisting and does not fly by the heat; but it does not possess any great surface, and it is very heavy. For the latter reason in many places the upper third of the tower used to be filled with the very hardest of coke; but this led to several accidents, by the coke taking fire when there was by chance no feed of acid on; there is also always some action of the acid on the coke, as shown, pp. 350 and 791. Most factories have given it up again, but it may be still in use here and there.

Silica in the form of quartz is frequently employed; but some descriptions of it are very liable to cracking in course of time, and filling up the gas-channels to such an extent that the draught, and with it the yield, is enormously impaired. Herreshoff (Amer. P. 335699; B. P. 1861, of 1886) employs nothing but pieces of quartz within the Glover tower. As these cannot be very well obtained in the regular shape for an ordinary lining, he keeps the lining a foot or so away from the side of the tower, and fills the space thus formed with quartz-sand. The lateral pressure due to this interior filling is resisted by suitable plates outside of the lead sides of the tower. The bottom of the tower is so constructed that it resists the action of hot, strong acid. These towers are said to be nearly indestructible, and to concentrate the acid up to 63° or 64° Bé. The acid from the Herreshoff towers is so free from iron and alumina that it is run directly into a platinum still or pan, and concentration is completed in an iron pan, the hot gases from the furnace passing under steam boilers. These towers have been in use ever since 1885 at the Nichols Chemical Co. and the General Chemical Co. (Chandler, in *J. Soc. Chem. Ind.*, 1908, p. 269).

Falding recommends quartz of a vitreous appearance, free from cleavage-lines and admixture with schist or other foreign matter. A little pyrites or oxidised pyrites does not hurt, but it must not be present in such quantity as to cause a flaw or to cause the quartz to "break down."

For packing the towers even broken glass or stoneware seltzer-water bottles with their bottoms knocked out have been found useful. One of the best materials for this purpose seems to be that supplied by the potteries at Bad Nauheim (Germany). It consists of almost pure silica, is burnt at the intensest white heat, cuts glass, and resists both any change of temperature and the prolonged attack of hot acids. Lining-bricks of this material cost £1, 10s. per ton; for packing the towers short open cylinders are made about 5 or 6 in. long and 4 in. wide (at £3, 10s. per ton). Formerly these were thrown in without any special care, but this is decidedly wrong; the cylinders should be put in in a regular way (see below). The Buckley Brick & Tile Co. also supply such "rings" for packing Glover towers. According to G. E. Davis this packing answers better than the coke-packing (which for Glover towers is most objectionable anyhow!), but the damper must be used more freely and the distribution of the acid must be more perfect than with coke.

Sometimes the Glover towers are simply packed with bricks, set on edge, in open work, as in a Siemens's recuperator. These bricks should of course resist the action of the acid. Blue Welsh bricks (p. 860) are frequently employed, and even some descriptions of common bricks seem to stand very well (*J. Soc. Chem. Ind.*, 1885, p. 33). But undoubtedly they are always acted upon more or less, and yield up more iron and alumina to the Glover acid than towers lined and packed with Volvic lava or quartz (see end of this Chapter).

At Stolberg (1902) it has been found that acid-proof bricks, made from ground clay-slate in the Ruhr district, stand much better in the Glover tower than fireclay cylinders. The hydrogen fluoride evolved in roasting blende most acts injuriously.

Brick-packing and also the ordinary cylinders have the drawback that they do not spread the acid or divide the gaseous current as well as denser kinds of packing.

Knab (Ger. P. 67085) promotes the unimpeded transit of the gases and prevents obstructions by a special kind of packing. He forms in the centre of the tower a column consisting of superposed cylinders. Each cylinder is provided with six slightly inclined earthenware tubes, arranged star-shape, and with their outer ends reaching into the brick lining of the tower. These stars are alternately arranged so that the pipes form a kind of steps, and four superposed stars fill up the whole section, the pipes of the fifth star lying exactly over those of the first star, and so on. The acid is thus compelled to run all round the pipes and to splash on to the pipes lying below. The pipes have different inclinations, in order to better divide the acid. [Such pipes will soon crack, and the whole apparatus must then collapse.]

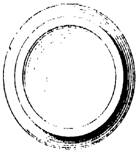
Saunders (Amer. P. 144928, of 1873) employs hollow glass balls with one or more openings.

Klencke (B. P. 25027, of 1908) rejects the usual coke or earthenware packing of Glover towers on account of the action of silicon fluoride contained in the burner gases on such packing. He employs a lead packing, and cools the gases previously by means of a tower without packing, so as to prevent the lead from melting.

Even when employing some other kind of packing than bricks (such as flints, cylinders, and the like) it is advisable to place just over the dome two courses of the same kind of bricks as serve for the lining, pigeonhole-wise, in order to divide the current of gas in a regular way. The packing, of course, must be done as systematically and carefully as that of the Gay-Lussac tower.

Lüty (*Z. angew. Chem.*, 1896, p. 645) states that the quartz (or flint) packing formerly used in Glover towers has been entirely replaced in Germany, first by acid-proof bricks or slabs, since about 1889 by cylinders, about 5 in. wide, 6 in. high, and ¾ in. thick. With quartz packing only 12 or 15 per cent. (after some mud has formed, only 10 per cent.) of the tower is empty and free for the reactions, with bricks about 35 per cent., with cylinders up to 58 per cent. Horizontal surfaces are much less active than perpendicular ones, which are in contact with constantly renewed acid. For this reason the success of the bricks and slabs is not so great as was expected, no more than that of the Bettenhausen "dividing-cones" ("Verteilungskegel"), as shown in Figs. 310 and 311. But the packing with ordinary cylinders has also led to many disappointments (pointed out, *e.g.*, by Guttmann in *J. Soc. Chem. Ind.*, 1903, p. 1331). This is easy to understand if the cylinders are glazed, or if they are placed in such a position that a system of continuous pipes is formed.

FIG. 310.



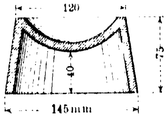
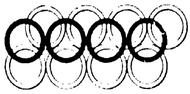


FIG. 311.

FIG. 312.



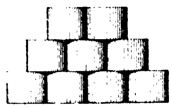


FIG. 313.

Lüty recommended cylinders 160 mm. high, 120 mm. wide, with walls 20 mm. thick, and a rough surface, placed in such manner that the joints are broken (Figs. 312 and 313[1]). They ought to be made of really acid-proof stoneware, not merely protected by a glaze which does not last very long. Even the best material, however, will be destroyed if improperly treated, especially by washing the tower with cold water, when its temperature is about 200° C. Instead of this, the tower should be allowed to cool down, or else hot acid or hot water should be employed for washing. When a tower has to be stopped for repairs to the chambers, the air should be prevented from entering, because the moisture contained in it, by diluting the acid soaked up by the cylinders, will in consequence of increasing the volume mechanically disintegrate these, even when no chemical attack of the earthenware takes place. The tower should not be washed with water at the beginning of the stoppage.

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[1] Niedenführ greatly prefers to this arrangement that which is shown in Fig. 332, where each cylinder is placed at the intersection lines of *four* other cylinders.

The *perforated plates*, on Lunge and Rohrmann's system, which have been described on pp. 659 *et seq.*, are not very well adapted for packing a whole Glover tower; in the lower part the holes would be too quickly stopped up by flue-dust, and they would be liable to crack there as well. But they can be employed very well in the upper half of the tower, the lower half being packed with bricks set edgeways, etc. This plan obviates an objection made to the Nauheim cylinders, viz., that in consequence of their comparatively large size the acid and the gases are not sufficiently brought into contact and the denitration is not very perfect.

An excellent application of these plates has been made in a case where it was necessary to bring about the denitration at the lowest possible temperature, in order to avoid losses by the ammonia present in the gas-sulphur (spent oxide) employed. A small tower of only thirteen layers of plates was put on the top of the ordinary Glover tower; the gases leave the latter at 90° C., and the plate-tower at 60° C. In spite of this slight difference of temperature and of the small height of the plate-tower, it was found to perform 80 per cent. of the denitrating work. Hence the plate-towers must be considered excellently adapted for this class of work, if they can be kept clear of flue-dust (which in the above case was retained by the old Glover tower). They must, however, not be flushed out while hot with cold water, which causes the plates to crack.

Great success has been attained by a special kind of packing, designed by Niedenführ on the plan of the Lunge-Rohrmann plates, and shown in Figs. 314 to 317. Here the acid is retained on the surface in a shallow layer, and on dropping down is always spread over fresh surfaces, without the danger of the cracking of plates and the stopping up of holes occurring with the ordinary Lunge plates.

Official information received from the Oker works in 1902 confirms that since 1900 the quartz-packing of the Glover towers has been replaced by "Lunge-Rohrmann" packing of the kind just described and by dishes, with entire success as to the concentration and denitration of the acid. The acid issues at a temperature of 150° to 160°, the gases at 75° to 80° C. The towers receive per annum 21,590 tons nitrous vitriol of 60° Bé. and 11,395 tons chamber-acid of 50° Bé. Some of the sets have two or three parallel-acting towers, 17 to 21 ft. high and 6 to 7½ ft. square; set No. V. has a tower 10 × 10 ft. square and 33 ft. high.

FIG. 314.

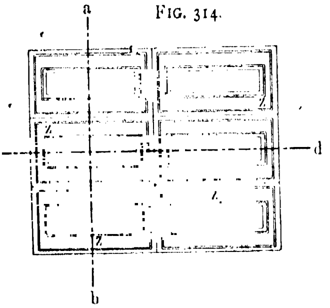
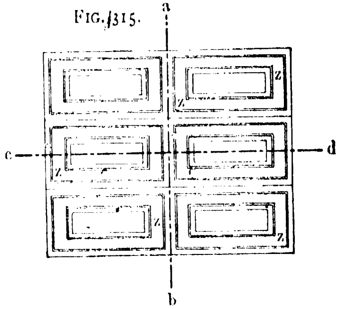


FIG. 315.



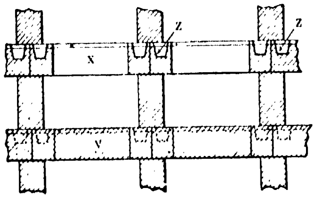


FIG. 316.

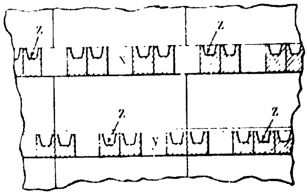


FIG. 317.

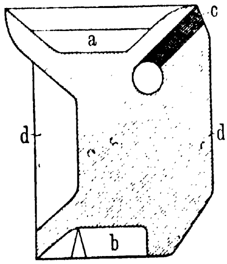


FIG. 318.

A new shape of stoneware packing for Gay-Lussac and Glover towers (or for distilling columns) is that described in the Ger. P. 158715 of Sauerbrey and Wünsche, and shown in Fig. 318. Each of the elements of this packing has a dished head, *a*, and a dished bottom, *b*; walls, *d d*, connecting these, with openings, *c*. This special shape is meant to compel both the gases and the liquids to travel in the precise way intended. The liquid runs in a thin stream over the surface, and the gases pass through it without any considerable pressure. These packing elements divide the space of the tower into horizontal layers of small cells, the top and bottom of which have perforations for allowing the gases and the liquid to pass from one layer to the other.

Rabe (*Z. angew. Chem.*, 1904, p. 78; 1906, p. 708; Ger. P. 148205) describes as packing for round or square towers "angular bodies," as shown in Figs. 319 and 320. They have principally perpendicular planes for the liquids to run down on, in a very thin layer, and his calculation makes them out to be ten times more efficient than clinkers of the ordinary shape, and weighing only one-thirteenth of their weight.

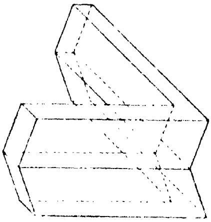


FIG. 319.

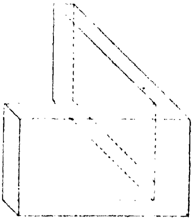


FIG. 320.

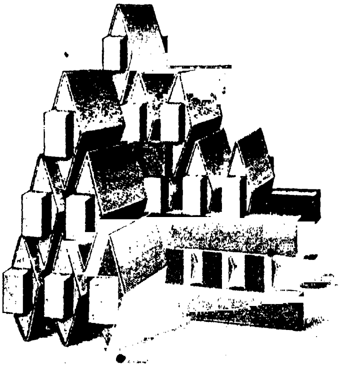


FIG. 321.

Lüttgen (Ger. P. 172445) employs for reaction towers, etc., a packing consisting of acid-proof stoneware bricks, placed edgeways, of quadrilateral or other section, with lugs in the centre of the ends, and bearers for carrying them on those lugs. Their shape is made clear by Fig. 321.

Evers (Ger. P. 172678) describes as packing-stones for condensation- and reaction-towers, horizontally placed stoneware discs, with concentric or spiral grooves on the upper and the lower side; the raised parts on any one disc corresponding to the grooves on the next higher or lower disc.

Wiltsch (Ger. P. 173612) employs cylinders or cones, with depressions on the upper and lower surface.

M. Liebig (*Z. angew. Chem.*, 1906, pp. 1806-1810) discusses various recently proposed forms of stoneware packing for reaction towers. He does not think it appropriate to replace the chambers entirely by such towers (cf. *suprà*, pp. 683 *et seq.*), as there is a certain time required for the union of SO_2, O and H_2O; but they are very useful as intermediate organs for re-mixing the gases between two succeeding chambers. Guttmann's ball packing (p. 680) is not so well adapted for large towers (apart from its extremely high price) as for small towers (for nitric acid). For the former a packing of clinkers on high edges of cylinders, of rhombic and ellipsoid bodies, etc., is preferable, especially Lüttgen's rhombohedric grate packing, Fig. 321 (p. 873), seems to him very good indeed, better than Scherfenberg's (p. 875); he quotes very good results he obtained with the former.

On the other hand, Feigensohn (*ibid.*, p. 2099) strongly opposes Liebig's recommendation of Lüttgen's packing, which he asserts to be inferior to Lunge plates and to various other recent systems, including his own rhombohedric bodies.

The Buckley Brick & Tile Company supply tiles of a special shape, according to a patent of Mackenzie and Gibson (*Chem. Trade J.*, 1908, xlii. p. 535).

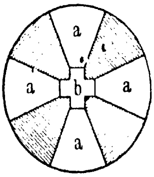


FIG. 322.

The Vereinigte Dampfziegeleien-Industrie A. G., Berlin (Ger. P. 191890), employs packing-bodies of the kind shown in Fig. 322, viz., balls with funnel-shaped holes, connected by a central channel, which cause the gases to assume a whirling movement and to come thoroughly into contact with the liquids.

The Chemische Fabrik Griesheim-Elektron (Ger. P. 218779) combine very thin, corrugated rings or prisms, which by themselves would be too weak for supporting the whole superincumbent burden with thick outside rings, etc., serving as strengthening for the former.

Peyton (B. P. 18831, of 1908) employs packing-bricks of circular shape, with elliptical or conical section, presenting a pair of upper and lower convex surfaces; on each surface there are four radial bearers.

Wilhelmi (Ger. P. 210759) shows a new kind of packing for acid-towers, by which triangular reaction spaces are formed.

Steinbrecht (Ger. P. 236880) provides the packing-bricks on more than two sides with round, oval, or angular nicks, serving for holding back the dust; after being used for some time they are taken out, cleaned from dust, and used over again in an inverted position.

The same inventor (Ger. P. appl. A12244) describes a packing consisting of cubes, the six sides of which are shaped as inverted pyramids.

Scherfenberg (Ger. P. 184893; B. P. 4366, of 1906; Ger. P. 239072) describes packing-bricks for reaction-towers, etc., of triangular, quadrangular, or polygonal section, with smooth or corrugated surfaces, provided with lugs for building them up crosswise.

Mackenzie (B. P. 17832, of 1906), in lieu of loose packing, provides Glover towers and analogous apparatus inside with solid walls, connected by bridges, the centres of one row of bridges being arranged above the centres of the row below.

Petersen (Fr. P. 382262; Ger. P. 209681) employs perforated V-shaped plates, as shown in Fig. 323.

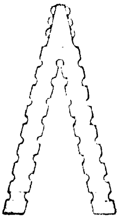


Fig. 323.

Green and the Huncoat Plastic Brick & Terra Cotta Co. (B. P. 28004, of 1910) pack the towers with tiles, recessed at the corners to take distance pieces by which they are built into successive floors or layers, each tile being provided with channels and troughs on the upper surface, and a series of ribs and channels on the under surface. Each floor is composed of a series of the blocks laid side by side and end to end, and the floors are so arranged that the main openings through the tiles on one floor are above the blank portions of the tiles in the next. The ascending gas is broken up and deviated by the channels and ribs on the under surface of the tiles, and while liquid is always lying in the recesses on the upper surfaces, it is being continually changed by the drip of liquid from above and its flow along the channels.

Olga Niedenführ (Ger. P. 183748) describes a tower-packing of the shape shown in Fig. 324, which explains itself. It is essential that the upright and horizontal parts should form an acute angle. Her Ger. P. 216342 shows tubes with projections at various points which fit into corresponding holes of the adjacent tubes, so as to produce a very good hold. Such tubes can be made up to 3 ft. high, and this greatly expedites the work in packing a tower.

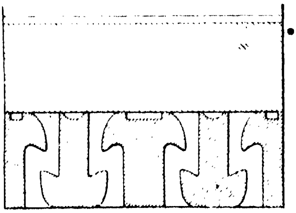


FIG. 324.

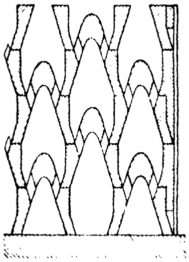


FIG. 325.

The Mayor, Alderman and Citizens of the City of Bradford, W. Wild and S. W. Shepherd (B. P. 19001, of 1906) pack towers with a series of crossed layers of vertical or inclined glass strips. The ends of these strips fit into the grooves of specially shaped bricks which are built into the lining of the tower. The depth of the glass strips is slightly less than that of the bricks, in order to allow a space between each two layers.

Guttmann (B. P. 4407, of 1907) employs channel-shaped pieces, provided with gas passages and draining-holes, and projections or shoulders, built up in a honeycombed structure, as shown in Fig. 325.

Pavlitzek (Ger. P. 229999) employs cubes with internal, diagonal, undulated partitions.

Wheatley, Sheldon & Tomlinson (B. P. 17472, of 1911) employ plates with projections at both ends, on which the next higher row of plates is resting.

Petersen (*Z. angew. Chem.*, 1911, pp. 972 to 975) discusses the examination of packing material for acid-towers, without bringing anything new.

Height of the Glover Tower.—In some cases it is preferred not to fill the tower to its very top, viz., if the gas is thus cooled too much; for then part of the first-formed aqueous vapour might be condensed again to the liquid state, dilution thus counteracting the concentration. The temperature of the outgoing gas is generally about 60° C.; some manufacturers prefer from 60 to 75° C. But if too much cooling must be avoided by leaving the upper part of the tower empty, that portion might be left out altogether and the tower be made so much lower. In fact, towers from 18 to 20 ft. high have recently been preferred to high ones. The height will, of course, depend upon the heat which the gas possesses when entering the tower, therefore upon the kind of ore burnt, upon the presence of dust-chambers, upon the length of way from the pyrites-burners to the tower, and so forth. According to numerous notes taken by me on this subject, the proper height for a Glover tower, under ordinary circumstances, seems to be from 20 to 25 ft. At one works, where two towers were erected, one 24 ft., the other 36 ft. high, it was found that the higher tower did no more work than the lower, so that the expense caused by the additional height, both in erecting and packing, seems to have been useless.

The distribution of the acid for feeding the Glover tower is effected precisely as in the case of the Gay-Lussac tower, either by reaction-wheels (*suprà*, p. 799) or by stationary overflows (p. 802). Acid-wheels of different descriptions are shown in our first edition, pp. 438 to 440, and in the second edition, pp. 587 and 588.

For very large Glover towers it is preferable to employ several spouts, running right across the top of the tower, with a number of lips on either side, each connected with a pipe leading to a hydraulic lute on the top of the tower. The principle of this apparatus, which will be noticed in the Niedenführ tower, Fig. 327, is the same as in the circular apparatus, Figs. 276 to 278 (p. 802), which is adapted to towers of smaller sections.

The regulation of the flow for the Glover tower is nearly always effected by hand, or else by the apparatus shown on

p. 807. Any apparatus for an absolutely constant supply of liquid would be out of place here, as the relative quantities of nitrous vitriol and chamber-acid vary, and must be regulated according to the state of concentration and denitration of the outflowing acid.

The cubic contents of the Glover tower worked by myself, and shown in our first and second editions, measured inside the lead without taking any account of the lining, the space underneath the dome, etc., for a daily consumption of 9 tons pyrites with 48 per cent. sulphur, amounted to 9 × 9 × 30 ft.—that is, to 2430 cub. ft. This for every ton of sulphur burnt daily amounts to about 550 cub. ft.; and this figure may be considered the proper one for the proportions of a Glover tower; at some of the largest works it is closely approached. At the Saint-Gobain Company's works the real working-space (*i.e.* that occupied by the packing moistened with acid) is from 70 to 160 cub. ft. per ton of pyrites, or, say, twice as much per ton of sulphur; and as the proportion of the working-space to the total space is not much more than 1 : 2, it may be said that the higher of the Saint-Gobain figures comes roundly to that which we have just stated as the normal one.

Description of Complete Glover Towers.

In the first and second editions of this book (2nd edition, pp. 576 *et seq.*) I gave the working-drawings and detailed description of Glover towers, such as were built from 1870 onwards, and as I had worked myself for a number of years. Many towers have been erected from those drawings, but I shall not repeat that description here, as it must be considered obsolete now, and I shall in place of this reproduce the designs of a modern Glover tower, as kindly supplied to me by Mr Niedenführ, carried out in practice with fullest success at a considerable number of works.

First I shall notice some recent descriptions of Glover towers found in literature.

Instead of the square section at first universally employed for Glover towers, latterly *circular towers* have come into use at many works. If lined with bricks, these are placed polygonally, unless suitable bricks, shaped to the proper bend, can be procured. In France the towers are usually lined with large blocks of Volvic lava, circular in section, and forming by themselves a substantial tower, although, of course, without any mortar, so that the lead shell is quite independent of them. Fig. 326 (from Frémy's *Encyclopédie chimique*, t. v. section i. p. 188) gives a horizontal section of one of these circular towers which serves for a set of chambers of 160,000 ft. capacity, and is constructed as follows:—It has a width of 6 ft. 9 in. and 23 ft. height, and rests on a block of masonry, set in cement and

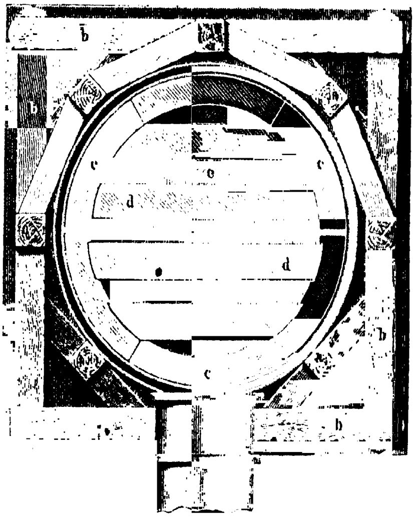


FIG. 326.

protected on the top by an apron of 7-lb. lead. On this are erected eight uprights, *a a*, mortised into octagonal horizontal frames at top and bottom. The uprights are 10 or 12 in. square, and are connected by two rows of cross-pieces, *b b*, provided with iron binding-bolts. The holding-straps for the lead are attached to the uprights. The leaden shell consists of four drums, which are burnt together in their places. The first two are 11 mm. thick (=25-lb. lead), the third 8 mm. (=18-lb.), the fourth 6 mm. (=14-lb.). This last drum is dressed inwards at the top edge, to be joined to the cover, which is suspended by means of straps from five railway-bars resting on the top frame. Until the lead drums are in their place, only five of the eight upright posts are put in, so as to leave a passage. Each drum is bevelled a little outward on the top edge, so as to form a seat for the next higher one; the joint is then filled with molten lead. The drums, before fixing, are left on the wooden cylinder on which they have been made, and are hoisted and lowered down into their place with the cylinder still in. The lava lining is provided for the first three drums only; the fourth is left naked, as the gases are here sufficiently cool not to injure the lead. There are eighteen pieces of lava, *c c*, six for each drum, in three courses with alternating joints, 10 or 12 in. thick; at Salindres they are 18 in. at the bottom, 12 in. in the middle, 8 in. at the top. The joints are made as thin as possible. The grate is formed by four or five sleepers made of lava, *d d*, as shown in the drawing; they are sometimes supported in the centre by a thin wall, *e*.

Circular Glover towers, even of very large dimensions, can be built without the applications of wooden or iron frames, the lead being stiffened by a few circular iron hoops (covered with lead), about 1 in. for each 5 ft. of their height.

The advantage claimed for circular Glover towers is that they require less lead for a given cubic space, and that the lead suffers less when it is bent in sharp corners. But while for Gay-Lussac towers these reasons may be accepted, it is, in the case of Glover towers, doubtful whether they are not counterbalanced by the much greater trouble and expense of constructing the circular lining.

Benker (1902) has built circular Glover towers of Volvic lava with a leaden shell which have stood for twenty years and are likely to stand as many more; also towers without a leaden shell, which are cheaper and simpler to make, but about the durability of which nothing can be said up to now. The towers are placed on such high foundations that the pipe from the dust-chamber has a rise towards the tower, and can be easily cleaned out every month. The grate is also made of Volvic stone, frequently also the packing, which is employed in pieces up to the size of a child's head. These towers are never stopped up with mud.

Guttmann (*J. Soc. Chem. Ind.*, 1908, p. 667) reports that in

England, too, Volvic lava towers are now made to stand by themselves, but sometimes a thin outer shell of 3 mm. lead is added to prevent the escape of fumes; iron hoops covered with lead hold the lava segments together, and sometimes even these are dispensed with. No wooden structure at all is required, since even reservoirs are dispensed with where automatic feeding apparatus are used.

Steuber & Co. (Ger. P. 227283) build acid towers without a lead shell, with double walls of acid-proof bricks. In order to protect the foundation against the acid, channels are made in it through which water is continuously run.

Lüty gives a design of cylindrical Glover towers (*Z. angew. Chem.*, 1896, p. 640) 10 ft. wide. The bottom is protected by a double layer of acid-proof tiles, 8 × 8 × 3 in. The sides are lined up to the lower side of the grate with arch-bricks, 14½ in. long, closely touching the lead, and leaving a clear space of 7 ft. 6 in. In this lining the inlet-pipe is built in, consisting of four large moulded pieces, with an inside diameter of 3 ft. 3 in.; into this another acid-proof pipe is introduced which on the outside is connected with the cast-iron gas-pipe by means of screw-bolts. On the floor two columns are placed, 8 in. square and 4 ft. 6 in. high; these, as well as the side linings, carry a grid, consisting of slabs 5 in. thick and 19 in. high, with intervals of 6·4 in., fixed by stone cubes put between the slabs. The packing begins above the grid with two layers of bricks, 13·4 × 3·14 × 7·87 in., the second layer crossing the slabs. Now follow two layers of bricks, 10 × 2 × 5·36 in., placed on edge. The lining behind the grid, and up to a total height of 21 ft. above the floor, consists of bricks shaped to the curve of the tower, 10 in. thick; above this to the top of the tower the lining is only 5·5 in. thick. The space above the grid up to the height of the outlet-pipe is filled with the cylinders described on p. 870, regularly placed in layers with broken joints, as shown in Fig. 313.

Later on (*Z. angew. Chem.*, 1897, p. 490) Lüty gives further details respecting Glover towers, especially advocating the erection of two towers acting parallel and dividing the gas from the burners. This was more particularly advocated by Niedenführ (*Chem. Zeit.*, 1897, p. 664), who also recommends a special kind of tiles for packing the towers which avoid the drawbacks mentioned by Lüty. Later on the employment of two paralle towers has been abandoned owing to the difficulty of an exact division of the gases, except for cases where two sets of burners each have their own Glover tower, both connected with the same set of chambers.

We now give drawings of a Glover tower (Figs. 327 to 332) designed and erected in a number of works by Mr H. H. Niedenführ, of Berlin, which embodies the latest experiences in that line.[1] On the foundation we notice, first, the strong horizontal timber frame on which the four wooden uprights are mortised. The frame is covered by wooden planking, cooled underneath by a network of brick channels lined with lead. On the planking we see the lead saucer of the tower itself 11 in. high, covered with stoneware slabs. The tower is 8 ft. 2 in. wide and 23 ft. high within the lead (this suffices for a daily make of from 10 to 15 tons H_2SO_4). The lining commences with 15-in. brickwork. From this springs a slotted arch, levelled at the top, where it has a thickness of 6 in. This serves as support for six courses of very open brickwork, *m*, running in alternate directions (as shown in the drawings) and sufficing for the deposition of most of the flue-dust. The wide spaces between the bricks are not easily choked up, and, moreover, this part of the tower is accessible for cleaning, as it is covered by a second arch, *n*, running in the opposite direction to the lower arch. Thus the tower can from time to time be cleaned out, by means of a short stoppage, without having to remove the whole of the packing, as is usually the case. On the second arch begins the proper packing, O, of Lunge-Niedenführ bricks, as shown in Figs. 314 to 317 (p. 872), and here the lining soon diminishes to 10 in. This packing occupies a vertical space of 8 ft., and is followed by a lining of 5 in. thickness, and 2 ft. 6 in. of packing, *p*, consisting of specially shaped dishes. The sectional plan at this level, Fig. 332, shows the way these dishes or cylinders are superposed (similar to the Gay-Lussac, p. 796, Fig. 270). The plan and sections of the top of the tower show the way in which the distribution of the acid is effected by means of the circular overflows *r*, lipped spouts *s*, and hydraulic lutes *t*.

As will be noticed, the dimensions and especially the working-height of this Glover are much less than was formerly assumed to be necessary, and this means less cost. This has become possible through replacing the old, fortuitously acting packings of flints or quartz, and the much too open packing of cylinders, etc., by a rationally graduated and systematically acting kind of packing, modelled on the original principle of the Lunge-Rohrmann plates, but avoiding the conditions which make these plates unsuitable for Glover towers (p. 871), at least for the principal part thereof. The splendid results obtained with this packing at the six systems working at Oker (p. 871) are convincing proof of its efficiency.

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[1] A paper by Lüty and Niedenführ (*Z. angew. Chem.*, 1902, pp. 244 *et seq.*) gives a reduced copy of these drawings.

Niedenführ (B. P. 1066, of 1904) *cools* the burner-gases before entering into the chambers by utilising their heat for concentrating the chamber-acid, or by special purifying devices, and purifies it, especially from arsenic, etc., by passing them through washers, filters, or the like. The denitration is effected by the action of such cooled sulphurous acid gases. A pressure generator is arranged before a special denitrating device, and between that and that part of the plant in which the acid is concentrated, in order to increase the relative efficiency of the denitrator and of the nitric acid in the chamber, and for decreasing the quantity of nitric acid necessary for carrying on the reaction.

A very important improvement seems to have been effected by H. H. Niedenführ, through his Ger. P. 140825, about which Lüty reports at length in *Z. angew. Chem.*, 1905, pp. 1255 *et seq.*, of which paper we now give an abstract (it is also abstracted in *Eng. and Min. J.*, 1905, pp. 634-635). It is well known to every expert that, in order to obtain the best results in acid-making, the work in the burners ought to be made independent of that in the chambers. This could not be properly done as long as the draught-producer was arranged at the end of the system; it should be placed between the burners and the place where the burner-gases are oxidised, beginning with the Glover tower. But a great difficulty to contend with in this case is the high temperature of the gases and, when burning smalls, the obstruction of the Glover tower by dust. Nor can the draught-producer be placed between the Glover and the first chamber, since the nitrous gases would speedily destroy any iron fan-blast, and stoneware fans in that place are also objectionable, as they require a higher driving-power and are very liable to breakage;

When placed behind the last chamber, the fan is also easily destroyed by the nitrous gases in their moist state. This objection could be avoided in those cases where the last portion of the chamber-space is replaced by Lunge's plate-towers, which deprive the gas of most of its moisture, so that the fan can be placed between the Lunge towers and the Gay-Lussac. These towers also present the best means for removing the excess of heat, produced by the higher intensity of reaction, by means of the dilute acid which is run down the towers. The least practical way of getting rid of the heat of the reaction, according to Lüty, is the placing of cooling-pipes hung up within the chamber (*vide* p. 649), nor does he think much of Benker's plan of passing the gases from the last chamber through a water-cooler. The afore-mentioned improvements have allowed of increasing the former normal production of lead-chambers, *i.e.* 3 or 4 kg. acid of sp. gr. 1·53 per cubic metre to 6 or 7 kl., of course apart from chambers combined with Lunge towers or the like. A real increase of that yield is now possible through Niedenführ's new invention, the principal feature of which is: dividing the functions of the Glover apparatus upon two towers, and placing the draught-producer between these. The burner-gases first pass through a concentrating-Glover, in which they give up most of their heat and are purified from dust, so that they cannot any more do any damage to the fan-blast; the latter, owing to the diminution of the volume of the gases by the cooling, has hardly any more work to do than when placed behind the chambers. The purified and cooled gases are forced by the fan-blast through the second, the denitrating, Glover into the chambers, and ultimately into the Gay-Lussac tower. The acid (nitrous vitriol) from the latter serves for feeding the denitrating Glover. If the denitration of the nitrous vitriol is to be complete, a little steam is introduced, and so much chamber-acid or even water is added that the strength of the acid feeding the second Glover does not exceed 1·619, or at most 1·65 sp. gr. In that case this acid still holds nitrogen acids to the amount of about 0·2 per cent. nitric acid of sp. gr. 1·33; it is now run down the first concentrating Glover, in which it is brought up to sp. gr. 1·71 to 1·73 and deprived of the last trace of nitrogen acids, and is now employed for serving the Gay-Lussac towers.

This system, in a plant for working-up 18 tons pyrites (44 per cent. S), where the dust-chambers were properly managed and a temperature of the gases of 400 to 420 was maintained, before they entered into the first Glover, permitted of adding in this considerable quantities of chamber acid for concentration.

The following advantages accrue from this way of proceeding. The work of the burners is made independent from that of the chambers; the latter may be worked with a minimum of draught without any bad influence on the burning work and on the composition of the burner-gas. Since the burners are working with uniform draught, more concentrated burner-gas can be obtained, say about 9 per cent. SO_2; the exit-gases from the Gay-Lussac then show about 4 per cent. oxygen, which is quite sufficient. The burners admit of much greater charges than formerly admissible, with uniform and very good results, say 0·5 to 1·0 per cent. S in the cinders. Niedenführ's system also admits of combining various kinds of burners, and working different descriptions of ore at the same time. At Roubaix, *e.g.*, he combined for one and the same set of chambers three sets of burners, one of which was worked with very bad blende, containing 10 per cent. lead, and the other two with pyrites, now and then with addition of galena, without any difficulty in the chamber process. Moreover a larger number of burners can be charged and stirred up at the same time. There is no blowing-out of gas from the burners. The chambers can be worked at a higher pressure than with the old system; the gases are thus brought into more intimate contact with one another, the formation of sulphuric acid and its separation are hastened. A set of tables, given in the original, shows that the temperatures within the chambers show but very slight variations in their whole length; we here give only an abstract of the observations, made in 6 places in set A (a factory in France, with 4 chambers), and 8 places in set B (in Austria, with 2 chambers):—

	In rear of Glover I.	In rear of Glover II.	Chamber 1.	Chamber 2.	Chamber 3.	Chamber 4.	In front of the Gay-Lussac.	Deg
A	308-323	105-110	71-80	49-61	38-40	24-33	19-22	(
B	410-423	87-94	83-91	61-67	...	...	28-34	,

These two plants have ordinary rectangular chambers, but the new system has also been applied to Meyer's tangential chambers (p. 622), with the same success.

The work done by this system is very great: from 9 to 11·5 kl. of chamber-acid per cubic metre; it is all the better, the higher and the narrower the chambers are made. The consumption of nitre in the factory A, for a prolonged time of work, was 0·6 to 0·7 parts nitric acid sp. gr. 1·33, for each 100 parts sulphuric acid sp. gr. 1·53.

The excellent results obtained by the application of his process to various entirely different systems of chambers have caused Niedenführ to apply for a patent for a tower-like shape of chambers, in which the gases travel from the top downwards, thus producing a more intimate mixture.

The original paper further gives sketches for a model set of chambers, as planned by Niedenführ, which is to combine all improvements and to produce sulphuric acid at a lower cost than ever possible up to now.

(In the discussion following the reading of this paper it was pointed out that already in 1877 the Freiberg factories, and later on American factories, worked with fan-blasts placed between the burners and the chambers. The novelty in Niedenführ's new system is the placing of the fans between two Glover towers, each of which has its separate function to perform.)

Niedenführ's Ger. P. 207765 proposes carrying out the separation of the denitrating and concentrating functions of the Glover in the same tower.

In *Z. angew. Chem.*, 1908, pp. 249 *et seq.*, Schmidl, who had introduced the division of the work of the Glover on two towers, as proposed by Niedenführ, reports on the results obtained thereby. He refers to the criticisms of that system by Neumann and others, which we have mentioned on a previous occasion (*suprà*, pp. 762 *et seq.*). In 1906, as stated by Niedenführ in *Z. angew. Chem.*, 1906, p. 61, twenty-eight works had already adopted his plan, and others were making preparations for it, among them the factory managed by Schmidl. That factory retained the nitrous gases by a Lunge tower, and after this by an ordinary Gay-Lussac, the former having 0·9, the latter 3·1 per cent. of the volume of the chambers. By feeding these with

150 per cent. of the daily production of acid at 60° Bé., he obtains in the Gay-Lussac an acid containing as much nitre as corresponds to 2 to 2½ per cent. nitric acid, 36° Bé. By running this down the Lunge tower, it comes up to 5½ per cent. nitric acid, and leaves the tower 59½° to 60° Bé. strong. This nitrous vitriol on being passed through the denitrating-Glover is always completely denitrated, and comes out at a strength of 57° or 58° Bé. The other, the concentrating-Glover, performs the concentration up to 60° Bé., not merely of the nitrous vitriol from the Gay-Lussac, but of so much more chamber-acid, that it amounts to 210 per cent. of the daily production. The burner-gases immediately before the Glover I. have a temperature of 500° and upwards; the gases leaving this tower, 115° to 100°, and they leave the Glover II. with about the same temperature; that of the denitrated acid flowing out of this is 100° C. In this tower about 14 per cent. of the total production of acid takes place. The chambers at that works produce 7 kl. acid of 50° Bé. per cubic metre, but would easily furnish 8 or 9 kl. if so much was needed, and in this case the Glover I. would also concentrate even more chamber-acid, since it would receive hotter gases. Schmidl further points out that Petersen (see p. 888), who works with blende, employs practically the same apparatus as Niedenführ, and in reality gets no higher results than this.

Petersen (*ibid.*, p. 1235) makes some remarks on Schmidl's paper. Schmidl replies, *ibid.*, p. 1456. Further remarks are made by Neumann (*ibid.*, p. 1746), Schliebs and Schmidl (p. 1747), none of them of any practical importance.

Nemes (*Z. angew. Chem.*, 1911, p. 392) says that Niedenführ himself had abandoned the application of two Glovers, as the division of the functions caused bad denitrification and bad concentration [?]. A reply to him was made by Petersen (*ibid.*, pp. 877 and 1811).

Ménard-Dez (Fr. P. 354073; *J. Soc. Chem. Ind.*, 1905, p. 1066) places behind the dust-chamber, first, a packed tower in which the gases are washed by sulphuric acid and cooled to a temperature not exceeding 500°. The products of the decomposition of sodium nitrate are introduced either before or behind that tower. Then follows a second packed tower in which dilute sulphuric acid is concentrated by the heat of the gases, and these are now passed through a series of cylinders, packed with copper-turnings, or with an oxide copper ore; the solution of cupric sulphate, here formed, is withdrawn for crystallisation. From here the gases pass into ordinary lead-chambers, and at last, in lieu of a Gay-Lussac tower, through packed cylinders, where the residual nitrous compounds are converted into nitric acid by means of air and water.

Petersen (*Z. angew. Chem.*, 1907, p. 1102; B. P. 27738, of 1906; Ger. Ps. 208028, 219829) effects an increased supply of nitre, as required for "intense" production (p. 639), by erecting a second set of Glover and Gay-Lussac towers, separate from the ordinary set, and fed with rather weaker acids than the usual strength, say 54° to 58° Bé., so that it can still in the Gay-Lussac absorb the nitrous gases, but gives them up again in the Glover to SO_2 without the necessity of any dilution or of the employment of particularly high temperatures. The nitrous vitriol coming out of this tower is denitrated by itself. The whole arrangement thus consists of the following parts:—(1) Glover tower, fed with nitrous vitriol 60° Bé. and dilute acid; (2) denitrating tower with nitrous vitriol of the second Gay-Lussac, 54° to 58° Bé.; (3) lead chambers; (4) Gay-Lussac of the second system fed with Glover acid 54° to 58°; (5) Gay-Lussac of the first system, fed with Glover acid 60° Bé.; (6) regulator. This is a very important apparatus, consisting of a tower fed with cold nitrous vitriol 55° Bé., which constantly circulates in this tower. It prevents any disturbance in the Gay-Lussac, as it keeps out the agents preventing the formation of the nitrous vitriol, viz. SO_2, steam and heat. The author discusses this at length, but we must refer the reader to the original. According to his Ger. Ps. 225196 and 225197, Glover acid of 57° Bé. is run through the outer Glover, where it gets up to 60°, and is now used for absorbing nitrogen oxides in the inner Gay-Lussac. The nitrous vitriol, here produced, goes to the inner Glover, where it goes down to 57° by the aqueous vapour coming from the first tower, and is used for feeding the outer Gay-Lussac. Or else the nitrous vitriol from both Gay-Lussacs is denitrated in the same Glover, and the first Gay-Lussac is fed with chamber-acid.

Petersen's Ger. P. 225198 describes a special way of denitrating the acids, obtained in two separate Gay-Lussac towers, by means of somewhat less concentrated acid, obtained in one of the Glovers. According to his Ger. P. 226793, the gases in the absorbing apparatus are treated with acid, previously brought into contact with nitrogen oxides for the purpose of oxidising any metallic proto-salt present. In case of using three Gay-Lussac towers, the acid coming from the second tower is pumped on to the third tower, and from this on to the first tower, which is placed just behind the chamber. Or else the gases and the acid in the last Gay-Lussac are passed through in the same direction, or the oxidation is performed by adding to the fresh Glover-acid part of the nitrous vitriol coming from the first Gay-Lussac.

Olga Niedenführ (Ger. P. 207760) also divides the Glover into two separate apparatus, viz., a cooler and a denitrator. The acid coming out of the latter is almost completely denitrated, and is hot enough to be concentrated to 60° Bé. by the burner-gases. On the other hand, in the upper, the denitrating space, excessive heating and consequent loss of nitre is avoided. Her Ger. P. 206877 provides a cooling passage half-way up the tower, which receives the rising vapours and returns the condensed liquid by means of special tubes.

Klencke (Ger. P. 219400) avoids the trouble caused in Glover towers by the presence of fluorine in the gases, which act upon the packing, by previous cooling in an empty tower, whereupon they go into a tower fed with dilute acid, and then into another tower provided with lead shelves.

Vender (Aus. P. 43749) denitrates nitrous vitriol by means of the hot gases, resulting in the combustion of atmospheric nitrogen.

Position of the Glover Tower.

At most works, quite properly, the Gay-Lussac and Glover towers are erected side by side, so that their tops are accessible by a common staircase, and even on the same level (in which case the Glover towers, being much lower, must stand on a higher foundation than the Gay-Lussac towers). It is unnecessary to point out how much the supervision of the work, the feeding of the towers, etc., is simplified by this plan. The position of the Glover towers being given between the burners and the first chamber, it follows that the Gay-Lussac is at the greatest possible distance from the last chamber with which it is connected; but this is all the better, as the gases have more time to cool and get dried in the long connecting-pipe. It is also an advantage that the nitrous vitriol has not to run very far, as it sometimes contains gas (NO), which impedes its free running. As a long pipe increases the friction of the gaseous current, it mostly involves providing chimney-draught or else a fan-blast for the chambers, which is certainly the best plan for all reasons (p. 753).

Working of the Glover Tower.

The Glover tower may be operated with only the nitrous vitriol itself running down in it, without any chamber-acid; but in that case it does not deprive the acid of all the nitrous compounds, but of the principal part only (down to about 0·2 per cent. of N_2O_3), and at the same time concentrates it to 152° Tw. This acid may now be used again in the Gay-Lussac tower for absorption; and thus a circulation of acid may take place between the two towers. There is in this process always a certain addition to the acid, as within the Glover tower itself, by the action of the sulphuric dioxide on the nitrosulphonic acid, free sulphuric acid is formed, as described on pp. 897 *et seq.*

However, the Glover tower is not usually fed (in the way just mentioned) with nitrous vitriol alone, except in the case of temporary disturbances. The apparatus is mostly so arranged as to be fed with a mixture of *nitrous vitriol* (or fresh *nitric acid*) and *chamber-acid*, in which case not only is the denitration completed, owing to the initial dilution, but a very acceptable secondary effect is obtained, viz., concentrating the chamber-acid up to 152° Tw., and depriving it also of the minute proportion of nitre which it generally contains. If the acid is not, as is usual in England, brought in the chambers themselves to 116° to 124°, but only to 106° Tw., it can still be concentrated to 144° without any difficulty in the Glover tower, even when the gas comes from a shelf-burner for pyrites-smalls and has therefore to be somewhat cooled in dust-chambers, on the supposition that the tower is placed close to the burners. That the denitration by sulphur dioxide becomes more perfect by dilution is a matter of course, according to the above-quoted researches of R. Weber, Cl. Winkler, and my own.

Where the leading-chamber makes very strong acid, which does not sufficiently dilute the nitrous vitriol, the Glover tower produces too strong an acid, which is incompletely denitrated and would injure the stability of the tower unless a little water is run down at the same time.

The stream of nitrous vitriol and that of chamber-acid are regulated entirely according to the degree of denitration and of concentration shown by the acid running off at the bottom of the Glover tower. The more chamber-acid is run through (that is to say, the greater the dilution), the easier will be a full denitration; the less chamber-acid is used, the more concentrated will the acid arrive below. There is, however, no difficulty in attaining *both* objects, viz., to get an acid completely denitrated and yet testing 152° Tw., if good pyrites be burnt, and if the burner-gas be employed as hot as possible, say 300° C. and upwards, by placing the tower close to the burners. In the case of poor ores or of smalls-burners with large dust-chambers, the denitrating action will also be complete; but the concentration cannot then be carried so far.

If it be assumed that the Gay-Lussac tower receives a quantity of acid equal to the total daily production, there will, of course, be just the same quantity of SO_4H_2 running down the Glover tower in the shape of chamber-acid, together with the nitrous vitriol, and therefore, according to bulk and weight, a little more of the chamber-acid, as this is more diluted. If the chamber-acid is on an average = 123° Tw., equal to 70 per cent. SO_4H_2, 117 parts by weight of the same correspond to 100 parts by weight of an acid of 152° Tw., = 81·7 per cent. SO_4H_2; or 100 vols. of the latter are equal to 128 vols. of the 123° acid, and the latter would be the proportion in which the two acids are mixed. The result would be a mixture of acids of 136° Tw. entering the Glover tower at the top, which can be fully denitrated by sulphur dioxide, especially when hot. If less Gay-Lussac acid has been used than the above, the mixture of acids entering the Glover tower will show a lower specific gravity than 136° Tw., and will be all the more easily denitrated.

During the first years of the working of the Glover tower it was generally assumed that *the acids must only be mixed inside the tower*, because during their mixture nitric oxide would be given off. On this principle was founded the mixing-apparatus described by me in my first publication on the Glover tower (in *Dingl. polyt. J.*, cci. p. 348), and the distributing-wheels with double outlet and separate distributing-chambers and pipes. But it follows from the calculation just made that a mixture of equal parts of acids, when chamber-acid of 123° Tw. is used and the daily make of acid is passed through the Gay-Lussac tower once a day, would be equal to 136° Tw. In an acid of this strength nitrososulphuric acid is sufficiently stable, at least at the ordinary temperature; and it is possible, and has been done in many places for years past, to mix the two acids before they enter the Glover tower, which greatly simplifies the distributing-apparatus. Even when only one-half of the total daily make of acid is used for absorbing, the mixture of this with the total chamber-acid still comes to 131° Tw., which is equally a safe strength. If, however, the conditions are more unfavourable in this respect, the dilution can no longer take place outside the tower. If, for instance, the chamber-acid is only 106° Tw. strong, 131 parts by weight of it correspond to 100 parts of acid of 152°; and if of the latter only half the equivalent is taken (that is to say, 100 parts by weight of acid of 152° Tw. to 262 parts of 106°), the density of the mixture only comes to 118°, at which strength nitric oxide begins to escape from a solution pretty rich in nitrososulphuric acid; but the above is an extreme case which rarely happens.

In these calculations the degree of saturation of the vitriol with nitrous compounds is not yet taken into account; the less the amount of acid used every day in the Gay-Lussac tower, the more will it be saturated with nitre, and there will be more danger of gas escaping from the nitrous vitriol when mixing it with chamber-acid.

The *temperature* of the acid running off from the Glover tower is usually between 120° and 130° C. (At Stolberg, in 1902, it was usually 120°, exceptionally up to 135°, the gases entering into the tower at 300°, sometimes up to 400°.) If the work is very much pushed, it may reach 140° or even 150°. In the few works where this happens, no bad consequences have been observed; but in one works I was told that a little more nitre was always used whenever the acid became hotter than 138° C. Still the observations made there were not sufficient to establish this result as certain, if all disturbing conditions be eliminated. The gas leaving the tower at the top has generally a temperature of from 50° to 80° C. (at Stolberg from 80° to 120°); it should not be above 60°, at which temperature cooling it before it enters the chambers is quite unnecessary.

Hegeler and Heinz (Fr. P. 341257) work the Glover tower in such a manner that it acts as a *producer of sulphuric acid from top to bottom;* furnishing hot concentrated acid, they protect the sides of the tower against an attack by lowering the temperature of the bottom part. For this purpose they inject part of the nitrous gases by means of a fan-blast into the burner-gases before entering the Glover tower. They assert that in this way they get the Glover acid up to 170° Tw. The same inventors (Ger. P. 184959) introduce part of the gases, coming out of the top of the Glover tower, again into it at the bottom, by means of a special pipe, provided with an arrangement for propelling the gases. This process intends a better utilisation of the nitrogen compounds and a reduction of the chamber-space by the more intimate mixture of the gases, and it prevents an excessive heating of the bottom part of the tower. The nitrous compounds thus pass several times through the tower and are more thoroughly utilised for the production of sulphuric acid, before they pass into the first chamber.

Glover Towers connected with Dust-Burners.—One of Bode's towers, working with dust-burners, had to receive the burner-gas after passing through a large dust-chamber. The gas, therefore, only reached the tower 152° to 180° C. hot; and the temperature on leaving it varied between 30° and 40° C. The hot acid running off showed between 96° and 110° C. When this tower was only employed for concentrating chamber-acid, it daily evaporated 6 tons of water and produced 2 tons 3½ cwt. acid of 144° Tw. from chamber-acid of 110°. This corresponds to a saving of coals for chamber-steam equal to 1½ cwt. per diem. When the tower was employed both for concentrating and denitrating, it supplied daily on an average 2 tons of acid of 144° Tw., and evaporated 9 cwt. of water; the denitration was perfect. The kiln-gas contained 7½ per cent. by volume of sulphur dioxide. Of course the above results are much less favourable than with the usual initial temperature of 300° to 400° C. Even in the latter case the temperature of the gas leaving the tower does not exceed 50° to 60° C. Such a hotter tower of 8·28 sq.m. section, according to Vorster (*Dingl. polyt. J.*, ccxiii. p. 411), in twenty-four hours evaporated 1400 kg. water; another tower of 4·55 sq.m. section, 1048 kg. water, the kiln-gas containing 8 per cent. by volume of sulphur dioxide.

Even when in Bode's Glover tower, by an accident, the percentage of the kiln-gas had gone down to 6 or 5 per cent. of sulphur dioxide, there was still complete denitration and an evaporation of 7 cwt. of water daily, equal to 1·7 ton of acid of 144° Tw. Bode calculates from this that even when calcining the poorest ores the Glover tower still remains a useful apparatus.

Hasenclever reported as early as 1872 (*Ber.*, 1872, p. 506) that the Glover tower had been successful in combination with his plate-burners; I have found the same in combination with Malètra's or other shelf-burners in a large number of works, at all of which, of course, there were dust-chambers.

At those works where sulphuric acid is made from *brimstone*, Glover towers are not so regularly employed as with pyrites-burners. The reason of this cannot be insufficient heat of the gases, as is proved by the practice of several large works where the Glover towers work perfectly well with brimstone-burners, and show all the advantages found elsewhere. Sometimes it is asserted that the higher value of brimstone acid as against pyrites acid is impaired by iron carried into it from the Glover tower; but this cannot take place except with an inferior description of packing material, and it is entirely avoided by confining the work of the tower to denitrating the nitrous vitriol, and taking the sale-acid from the chambers or from lead pans put over the burners. The real reason for the comparative neglect of the Glover tower at brimstone-acid works is this, that many of these works are of small extent and cheaply laid out, and are managed with insufficient care, so that their owners would rather lose nitre and sulphur than incur the expense of erecting and the trouble of working Glover towers. At several large American works I found Glover towers working most satisfactorily with brimstone burners. In these cases the heat of the gases was first utilised for concentrating chamber-acid up to 140° Tw., or even (in H. Glover's sulphur-burner, *suprà*, p. 403) to 168° Tw., after which the gases entered the Glover tower and there produced acid of 150° Tw., with a temperature of from 126° to 130° C., sufficient in quantity for amply supplying the Gay-Lussac tower.

At larger works, possessing a number of Glover towers, it is a frequent and convenient arrangement *to work them in different ways*, viz., partly for making acid for the Gay-Lussac towers and partly for concentrating acid for the saltcake-pans. The first should be as strong as possible, and need not be entirely denitrated; it can be obtained in this state by feeding but little chamber-acid along with the nitrous vitriol. There is thus a constant interchange of acids between the two kinds of towers; but the Glover tower makes a good deal of fresh acid, so that part of it must at all events be employed for other purposes.

The acid for decomposing salt, or for sale, etc., on the other hand, should be entirely denitrated, and need not be so strong as the former; for this purpose much more chamber-acid is fed along with the nitrous vitriol.

We have already (p. 858) pointed out the *various functions* which are fulfilled by the Glover tower. The object for which it was first constructed, the *denitration of the nitrous vitriol*, that is the recovery of the "nitre" from this and the restoration of it to the chambers, is carried out by this means in the most perfect way and without any trouble. It is easy to work it so that the acid at the bottom contains even a slight excess of SO_2 (which is compatible with a very slight percentage of N_2O_3); nor is there any very high temperature required for it, especially when the nitrous vitriol is diluted with chamber-acid. In fact at some works the heat of the pyrites-kilns or the sulphur-burners is previously utilised for concentrating the acid, and the gases only then enter into the tower, where they perform the work of denitration, together with some little concentration, and are cooled down to the proper temperature for entering into the chambers. This plan is especially recommended for works where much acid is sold or is further concentrated to "rectified oil of vitriol," for which purpose the acid concentrated in the Glover tower is too impure (see below). This case also arises when burning arsenical ores, where the gases, in order to deposit the large quantity of flue-dust, have to pass very long channels (pp. 545 *et seq.*).

That the fear of losing any nitre in the Glover tower by reduction to nitrous oxide or nitrogen is totally unfounded, has been proved before (pp. 854 *et seq.*). Far less nitre is consumed in the manufacture of sulphuric acid than before the introduction of the Glover tower; and the change has in most cases been so sudden that it seems impossible to overlook this evidence.

The second principal function of the Glover tower is that of *concentrating* chamber-acid, which is intimately connected with two other functions: *cooling the gases* and *supplying part of the steam* for the chambers. The concentrating action of the Glover tower was first studied in detail by Vorster (*Dingl. polyt. J.*, ccxiii. p. 413), but he neglected the acid brought over with the burner-gas as SO_3 and that formed within the tower itself. Both these sources have been taken into account in the investigation of Scheurer-Kestner (*Bull. Soc. Chem.*, xliv. p. 98). From his analyses of burner-gases it appeared that these contained up to 9 parts of SO_3 to 100 SO_2; the average was about 3·5 parts. As there is enough water even in the air and the pyrites to hydrate the SO_3, it is sure to be retained in the Glover tower. He further shows the mistakes committed by Vorster in his calculations, from which the latter had concluded that very little acid was newly formed in the tower; and he opposes to this not merely the practical experience, according to which the introduction of a Glover tower saves from 10 to 20 per cent. of chamber-space, but also some special large-scale experiments made with an actual tower at the Thann acid-works, by carefully measuring for some weeks the excess of acid coming out from the tower over that going in. Thus it was found that the Glover towers made 15·7 to 16·3 per cent. of all the acid produced in the manufacturing apparatus. To this should be added the acid volatilised or mechanically carried away from the towers into the chambers, which was (only partially) estimated by measuring that which condensed in the connecting-pipes, and which amounted to 2 or 2½ per cent. of the total make, bringing the action of the towers to 17 or 19 per cent. This was entirely proved by the result of prolonged working on the large scale; for the same set of chambers which had previously made 6 tons of O.V. in twenty-four hours, made 7·28 tons, or 17·5 per cent. more, after adding a Glover tower to the apparatus.

Hence the concentration observed in the Glover tower is to a great extent only an apparent one; it is not merely due to volatilisation of water, although this also takes place to a considerable extent, but also to the formation of very much H_2SO_4, which dissolves in the acid used for feeding and raises its strength.

In a previously quoted paper (*Bull. Soc. Ind. Mulhouse*, 1889, p. 267; abstracted by me in *Z. angew. Chem.*, 1889, p. 275) Sorel has tried to follow the functions of a Glover tower, so far as they refer to the *formation of fresh sulphuric acid*, by elaborate calculations. We must omit the greater part of these, as he at the outset commits several grave errors which modify some of his figures to the extent of four or five times the real values. This refers especially to Sorel's calculation of the number of times the nitrous gases enter into reaction during their passage through the Glover tower, and the time occupied by each such reaction; we shall, therefore, substitute for these a new calculation, based on the figures to be given later on, indicating the real quantities of nitre supplied to the tower in one shape or another at a well-managed works. We may assume that for each 100 parts of sulphur burnt in twenty-four hours there is in ordinary cases supplied to the chambers the equivalent of 10·25 parts of commercial nitrate, of which about $\frac{5}{7}=7{\cdot}32$ parts are in the shape of nitrous vitriol, and $\frac{2}{7}=2{\cdot}93$ parts in that of fresh nitric acid. These would yield the following quantities of oxygen for each ton, say 1000 kg., of sulphu burnt, on being reduced to nitric oxide:

73·2 kl. 96 per cent. nitrate as

$$\text{nitrous vitriol yield } \frac{73{\cdot}2 \times 8 \times 0{\cdot}96}{85} = 6{\cdot}61 \text{ kl. oxygen.}$$

$$\text{29·3 kl. ditto as nitric acid yield } \frac{29{\cdot}3 \times 24 \times 9{\cdot}6}{85} = 7{\cdot}82$$

$$\text{Total } 14{\cdot}43$$

Now each 16 parts of oxygen oxidise 32 parts of sulphur, entering the tower in the shape of SO_2, to H_2SO_4. Hence the above 14·43 kl. of nitric oxygen will produce sulphuric acid from 28·83 of sulphur, if its action is exerted only once. In reality, however, up to 250 of the total 1000 S are converted into H_2SO_4 within the tower, which certainly includes the SO_3 carried over from the kilns; but as this on an average does not exceed 3·5 per cent. of the total S, we shall be safe in assuming that 200 kl. S, as SO_3, are actually oxidised within the tower, so that 200 − 28·8 = 171·2 kl. of S have been oxidised by renewed action of the nitrous gases. Considering further that the nitric acid is reduced to NO, and that in the further reactions this transfers upon SO_2 only as much oxygen as its equivalent of nitrous vitriol, the total oxygen transferable by each single action of the nitre present is only 6·61 + 2·21 = 8·82 kl., equivalent to forming sulphuric acid from 17·64 kl. sulphur. There must, hence, have been $\frac{171 \cdot 2}{17 \cdot 64}$, or, roundly speaking, *ten subsequent transfers of oxygen* upon SO_2 within the Glover tower after the first action of the nitre introduced.

We can also calculate the *time* occupied by each such transfer. The cubic contents of an ordinary Glover tower, counting the space within the lining from the surface of the grate to the top, varies from 180 to at most 300 cub. ft. per ton of sulphur burnt in twenty-four hours. If we take the very usual capacity of 200 cub. ft., and deduct 50 per cent. for the packing (which is probably below the truth), and if we further assume that the denitration is practically complete halfway down the tower (which is decidedly allowable), we get $\frac{200}{4}$ = 50 cub. ft. as the real empty space within which the acid-forming reactions take place, or slightly under 1·5 cb.m. Now the volume of gases given off by the combustion of 1000 kl. of pyrites-sulphur in a properly conducted operation is, as shown on p. 559, about 8144 cb.m., calculated for 0° and 760 mm. pressure. From this we must make a slight deduction for the gases taken out by the formation of H_2SO_4, say, up to the middle of the denitrating zone, equal to one-tenth of the total SO_2 = 70 cb.m., and the corresponding quantity of oxygen, equal to 35 cb.m., leaving 8039 cb.m. at 0° and 760 mm. pressure, or, roundly 8000 cb.m. As the average temperature of the denitrating zone is about 90° C., the above quantity of gases in reality occupies a space of about 10,700 cb.m., or $\frac{10{,}700}{1 \cdot 5} = 7107$ times the active space, that is the denitrating zone, of the Glover tower. Hence the sojourn of the gases within that space is $\frac{24 \times 60 \times 60}{7107}$, or as nearly as possible twelve seconds. But we have seen that there are eleven successive actions of the nitrous gases upon SO_2 within the tower, so that each of these, consisting, according to the older theories, of an oxidation and a reduction, or, according to the modern theory to be developed in the next Chapter, of the formation and decomposition of nitrososulphuric acid, cannot require much more time than one second.

We may draw another important inference from the established facts. The usual allowance of chamber-space per lb. of sulphur burnt in twenty-four hours is 20 cub. ft., or 44,800 cub. ft. per ton of sulphur. Of this ton, one-fifth is oxidised into sulphuric acid in the Glover tower, leaving four-fifths for the chambers. This means that 50 cub. ft. of active Glover-tower space, as defined above, make acid from 0·2 ton of sulphur, or 1 ton of sulphur here requires 250 cub. ft., whilst 44,800 cub. ft. of chamber-space make acid from 0·8 ton of sulphur, or 1 ton in this case requires 56,000 cub. ft. In other words: *the denitrating zone of the Glover tower makes more than 200 times more acid than an equal cube of chamber-space.* If we take the minimum chamber-space allowed at most English or German alkali-works, viz., 16 cub. ft. per lb. of sulphur = 35,840 cub. ft. per ton, this still means 44,800 cub. ft. for the acid really made within the chambers, or only $\frac{1}{180}$ of the activity of the Glover tower.[1]

Raschig (*Z. angew. Chem.*, 1909, p. 1183) confirms my estimate of the share of the ordinary Glover tower in the production of sulphuric acid, and quotes results obtained by Quincke at Leverkusen to the same purpose.

We shall now better understand why I recommend replacing a large portion of the chamber-space by columns acting in a similarly energetic way as Glover towers (pp. 657 *et seq.*).

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[1] These calculations are more correct than those I have given in the *Z. angew. Chem.*, 1889, p. 388, on the basis of Sorel's somewhat doubtful data and altogether wrong calculations.

This enormous action of the Glover tower is explicable on the assumption that the nitric oxide set free in the lower parts of the denitrating zone, according to the equation

$$2SO_5NH + SO_2 + 2H_2O = 3SO_4H_2 + 2NO,$$

is fixed again in the upper parts by the reaction:

$$2NO + 2SO_2 + H_2O + 3O = 2SO_5NH;$$

the nitrososulphuric acid thus re-formed on descending into the lower regions is denitrated again, and the NO, thus flying backwards and forwards, incessantly and quickly transfers oxygen upon the sulphur dioxide arriving in the shape of burner-gas. This action, which of course equally takes place in the chambers, is in the Glover tower immensely aided by the continuous mixture of the gases and their constant shocks against surfaces wetted with nitrous vitriol. The very large amount of heat produced by the chemical reactions cannot give rise to any considerable elevation of temperature, as the heat is expended in evaporating water from the acid trickling down, and concentrating this acid, as already pointed out.

If the tower be too high, and if the top be kept too cool (which will depend upon the former), much less than the above calculated work will be done in it. In this case there will be a considerable condensation of the steam, generated below, in the upper region of the tower; this will facilitate the denitration near the top itself, and the NO here generated will be carried over into the chamber without performing the above-described multiple work. Experience has indeed long ago shown that Glover towers ought not to exceed a certain height (25 or at most 30 ft., *cf.* p. 877) to do the best possible work, both for evaporation and for forming new acid. But Sorel, in my opinion, goes very much too far in advising that the Glover towers should be kept as hot as possible, and should be fed with as concentrated an acid as possible. He looks at one side of the question only, and that decidedly the less important one, viz., that there should be as great a production of acid as possible within the Glover tower, by retaining the nitrous compounds within it a very long time. He neglects two other considerations of much greater importance: that by his mode of conducting the process the *denitrating* work is greatly impaired, so that the acid issuing at the bottom carries away very sensible quantities of nitre, and that by the great heat of the gases and the concentration of the acid, the life of the tower is very much shortened. Sorel's plan interferes both with the complete denitration of the nitrous vitriol, and also with the important action of the Glover tower for bringing the chamber-acid just up to the strength required for decomposing salt, etc. (say 140° to 145° Tw.), merely in order to force rather more SO_2 through the chambers than they can otherwise manage to oxidise; but this object does not seem worth incurring the serious drawbacks just mentioned.

In order to make the burner-gases enter into the Glover tower at a *high temperature*, Hartmann & Benker (Fr. P. 196703) employ a relatively small dust-chamber, with a grid charged with broken bricks, pumice, or the like, through which the burner-gases travel from the top downwards. When the purifying material has become useless, it is removed by an opening below the grid, provided with a damper, without interrupting the process.

The United Alkali Co. (B. P. 1746, of 1907) arrange for the same purpose, in the flues leading to the Glover, plates charged with electricity, which retain the flue-dust and other impurities; these are from time to time removed.

Olga Niedenführ (Ger. P. 206877) cools the gases in the middle part of the tower by means of cooling-pipes arranged about half-way up the tower, without at the same time cooling the acid running down.

An interesting application of the Glover tower is that for utilising the nitrogen acids remaining in the *waste acid from the manufacture of nitrobenzene and nitroglycerine*; these are used in some works for running down in the Glover tower.

The following *drawbacks* are connected with the Glover tower, the first of which is, however, only temporary, and much less felt where there is no coke-packing in the Glover, but only in the Gay-Lussac tower. This coke communicates to the acid, especially at the beginning, a *brown colour* (due to organic substances), which is quite immaterial to its technical application, but injures its sale. After a little time this ceases, and the acid running away from the Glover tower is then as clear as water, and, on account of its strong refraction of light and oily appearance, is compared by the workmen to "gin."

The contamination with *iron* is permanent, and is somewhat stronger than in acid made from the same pyrites in ordinary chambers, simply because the tower at the same time serves for keeping back the flue-dust. According to Hasenclever, his Glover-tower acid contained 0·05 per cent. of iron (*Berl. Ber.*, 1872, p. 506).

Besides iron, the Glover-tower acid frequently contains considerable quantities of *alumina*, of course in proportion to the resistance of the lining and packing-material to the action of the acid, and also of arsenic.

The flue-dust and the sulphates of iron and alumina are often formed in such large quantities within the tower that it cannot be worked for any considerable time without being washed down occasionally by a strong jet of water. But in the long run this is not sufficient; the interstices get filled up with hard crusts, and the tower must be stopped for repacking, which is a very troublesome and expensive operation. It is hence advisable to go to some extra expense for the best obtainable lining and packing-material.

Where the Glover-tower acid is only used, apart from the service of the Gay-Lussac tower, for decomposing salt, for manufacturing manure, and for many other purposes, its impurities are of no consequence. But it cannot be used for such purposes where those impurities would be troublesome, and especially not for higher concentration to "rectified O.V." in glass or platinum retorts, as then hard adhering crusts of ferric sulphate are formed. Even then the use of a Glover tower need not be relinquished, but it must be either treated only as a denitrator, the heat of the burner-gases being *previously* utilised for concentrating acid (*cf.* pp. 439 and 542 and Chapter IX.), or else the acid required for the manufacture of rectified O.V. and similar purposes is taken out of the first chamber without passing it through the tower.

With Glover towers constructed on the Herreshoff system (p. 867), that is, with quartz lining and quartz packing, there is no alumina in the Glover acid, but the iron and arsenic derived from the flue-dust still remain as impurities, so that there cannot be much difference as regards the crusts formed in platinum stills.

An interesting application of the Glover tower is that for *utilising the waste acids from the manufacture of nitrobenzene and nitroglycerine.* At the Schönebeck works, and in many other places, these acids are run down in the Glover tower and are thereby denitrated.

Denitration by Other Means.

The proposal of Garroway (B. P. 1673, of 1883) to effect the denitration and concentration of the acid without a Glover tower, by means of stoneware vessels placed in the gas-flue between the burners and the first chamber, seems to offer very little prospect of success.

Windus (B. P. 367, of 1882) proposes, instead of denitrating the nitrous vitriol in Glover towers, to do this by agitating it within the chambers, and promoting the disengagement of the gases by producing a vacuum. The agitation is to be produced by mechanical means, or by allowing thin jets of acid to fall into the acid at the bottom of the chamber. It is unnecessary to point out the impossibility of denitration by this procedure.

Der Norske Akt. f. Elektrokemisk Ind. and Halvorsen (Fr. P. 363157) dissolve nitrous vitriol in an excess of strong sulphuric acid, add a little water and an oxidiser, such as MnO_2, PbO_2, CrO_3, or a chromate. The product is distilled in iron retorts, to obtain nitric acid, and the residue electrolysed to recover the oxidiser, thus:

$$Cr_2(SO_4)_3 + 6H_2O = 2CrO_3 + 3H_2SO_4 + 3H_2.$$

Salessky (B. P. 20131, of 1910; Ger. P. 232570; Fr. P. 419609; Swiss P. 52712) states that the denitrating process in the Glover tower is never assisted, but rather impeded by the presence of SO_2 in the gases, since the reduction may go as far as N_2O. He therefore denitrates with air only, which is heated to about 200° and blown by means of a small fan into the Glover tower, which in this case does not receive the gases from the burners, and is fed with water or weak sulphuric acid. His B. P. 20131, of 1910, prescribes supplying the nitrogen oxides, before they reach the chambers, in an enclosed space with air, to such an extent that they are as much as possible oxidised into nitrogen peroxide.

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CHAPTER VII

THE CHAMBER-PROCESS

Starting the Chambers.

Covering the Chamber-bottom with Acid.—In order to start a set of chambers, first of all the chamber-bottoms must be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into its upstand, as here an hydraulic seal is required to keep the gas within the chamber. Enough liquid for the sides just to dip into it is sufficient; for as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic seal is constantly improving. However, for reasons to be stated hereafter, it is preferable to make the depth of acid as great as possible from the outset. Only in extreme cases *water or very weak acid* should be taken for luting the chamber; acid should rather be bought elsewhere at some expense to avoid this. If it can be done, the proper thing is to bring up the bottom-acid at once to at least about 90° Tw., better 100°. If this cannot be effected, this strength ought at least to be approached as nearly as possible. The reason why starting a chamber with water or very weak acid should be avoided is, that otherwise the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead.

Even if all the nitric acid freshly supplied were decomposed by sulphur dioxide before reaching the bottom, the presence of water or very dilute acid in large quantity would cause the new formation of large quantities of nitric acid from the lower oxides of nitrogen (N_2O_4, N_2O_3, and NO), and, on the other hand, of nitrogen protoxide, N_2O; there would thus be a great loss of nitre in both shapes, apart from the action of the lead, and the reactions within the chamber would be quite irregular.

Altogether the chamber-process only goes on properly when there is an abundant quantity of pretty strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is even preferable to start a chamber dry to starting it with water; but otherwise a layer of about 4 in. of acid on the bottom of such chambers is preferred.

Supposing the chambers to be luted with acid, and the burners to be heated up, so that they can be charged, the connection between them and the chambers is made and the *burner-gas* allowed to enter. Of course sufficient draught is given and nitric acid admitted at once, but at first no steam, in order not to dilute the bottom-acid too much. The *nitric acid* is introduced precisely in the same way as later on, either as vapour or in the liquid form. At first about three or four times as much is put in as is necessary afterwards, because there must be a stock of nitre-gas collected in the chambers, which subsequently needs only to be renewed so far as any loss is suffered. Liquid nitric acid can be introduced much more quickly than gaseous, since the latter depends upon the heat of the burner-gas working the nitre-oven; but running too much nitric acid at once into the chamber must be avoided, since it might not be decomposed entirely before reaching the bottom. This can hardly happen when introducing it through the Glover tower. At the beginning from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, must be employed to 100 parts of sulphur; and this must be continued till the last chamber turns yellow; then the quantity is gradually diminished till the proper point is reached.

MacCulloch (*Chem. News*, xxvii. p. 136) prescribes starting the chambers by admitting steam and nitre-gas from the steam-column (*cf.* p. 849) for five or six hours before the burner-gas is admitted. In that case, he says, the chambers work well from the first, and in one instance showed acid of 1·65 at the drips already in twelve hours. This may be so; but that process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, *steam* is admitted, usually on the second day, but at first with great caution. Then all the factors of acid-making are at work, and the same rules are now valid as for the ordinary process. If everything is in proper order, and if plenty of nitre is used (which is all retained in the Gay-Lussac tower), a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

We must also take into account the opposite case, viz., *when a set of chambers has to be stopped for repairs.* It may be necessary to do so for one or two days, and it is, of course, most important to be able to go on again as quickly as possible, without losing too much nitre. If the proper precautions are neglected, it is possible that so much nitric acid is produced that the chamber-lead is seriously acted upon. To avoid this, we must proceed as follows:—First of all, the pyrites-burners are stopped; no fresh charge is put in, and all openings are closed as tightly as possible. Next to this the supply of nitre is stopped, but that of steam is continued, so long as the gas of the last chamber shows any outward pressure. When this has ceased, and there is, on the contrary, some inward suction, the outlet damper is closed, and air is allowed to enter at some lute, manhole, sight, etc., to avoid forcing-in of the chamber-walls by the atmospheric pressure. Even now a good deal of acid is produced, as proved by the action of the drips; but the steam should be shut off as soon as the drips go down to 100° Tw. When the drips cease to act all openings are shut. If the burners are started again within three days from the stoppage, it is only necessary to put on a good supply of nitre in order to get the chambers to work again; the regulation of the steam must, however, be as carefully attended to as when starting a new set of chambers.

Supply of Air.

The object of a regular chamber-process is of course this:—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. We may add at once, as less decisive, but still of importance, that the chamber-acid should be as strong as is compatible with the two conditions just stated and with preventing damage to the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points, some of which have already been treated of in detail, whilst others will be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brimstone, follows as a matter of course; with pyrites it is much more difficult (*cf.* also pp. 442 *et seq.*).

2nd. *Proper Composition of the Burner-gas.*—This also has been treated of in the 4th Chapter; and we will here merely repeat that the proper composition of the burner-gas almost entirely depends upon the regular supply of air produced by proper *regulation of the draught.* We have already seen (p. 452) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. But at the chambers themselves this must equally be looked to, by means of the man-lids in the top, or the test-plugs (p. 701), or by pressure-gauges or anemometers (pp. 701 and 767). Generally, the following rules may be laid down as a rough guidance:—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue in force whenever a plug is opened. In the middle chamber the gas should be pretty nearly in equilibrium with the outer air; in any case there should be rather a little outward pressure than any inward suction. In the last chamber there may be some, but very little, inward suction; and behind it, but before the damper, the suction should be very perceptible. The Rhenania works (1902) keep some pressure throughout the chambers, diminishing gradually from front to back, the suction beginning only behind the Gay-Lussac, and this is also done at other well-managed works known to the author. Knapp compares the chambers to a lake traversed by a river: the speed of current at its inlet is diminished in the interior of the wide basin so as to be almost imperceptible; but at the outlet in the narrow draught-pipe it again comes out with the same strength as at first. Payen's *Précis* (i. p. 318) states the speed of the gas within the chambers to be 8 to 10 in. per minute. *Cf.* also Niedenführ's measurements of pressures, p. 677.

Generally, it may be said that the draught must be sufficient o cause a proper working of the burners and the proper comosition of the gas, but *no more than this.* The draught should e observed not merely by practical indications, but by testing he burner-gas for SO_2 and the exit-gas for O. The rule given an here be stated more precisely in this form:—There is so nuch draught given that the burner-gas from brimstone pproaches a percentage of 11 per cent., that from pyrites 8 per ent. SO_2, as far as circumstances permit, and that the gas ssuing at the end still contains 5 or 6 per cent. of oxygen.

A most important control of the working of the chambers, o far as the draught is concerned, is exercised by *testing the xit-gases for oxygen*, as has been described (p. 578), and will be nentioned later on in this Chapter. But there is no agreement n the question as to what is *the proper percentage of oxygen in hamber exit-gases.* Only so far there is general agreement that certain excess of oxygen is required, over and above the heoretical quantity, in order to promote and hasten the egeneration of nitric oxide to nitrous acid, etc. Bode *Beiträge*, p. 15) assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen the yield had been quite as good as, and the consumption of nitre even a shade better than, at 6 per cent. According to Hasenclever (*Hofmann's Report*, i. p. 370), in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from those quoted (*suprà*, pp. 556 and 558) are:—for brimstone,

10·65 per cent. by volume of SO_2,
10·35 " " " O,
79·00 " " " N;

for burning pyrites,

8·80 per cent. by volume of SO_2,
9·60 " " " O,
81·60 " " " N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas = 6 per cent. He has, however, proved that the oxygen in the *burner-gas* is considerably less than according to the above calculation, probably owing to the formation of SO_3 (p. 565).

The above is not universally accepted. Vogt contends (*Dingl. polyt. J.*, ccx. p. 105) that there ought to be only 3 or 4, never above 5 per cent. oxygen in the escaping chamber-gas; oxygen beyond 5 per cent. he calls "very bad work." This opinion is shared by some, but not by many, other practical men. The other extreme is found at a large alkali-works visited by me, where it is believed that the best yield of sulphuric acid is obtained with 10 per cent. of oxygen in the exit-gas, certainly with a somewhat larger consumption of nitre than when 5 or 6 per cent. of oxygen is adhered to (4 per cent. of $NaNO_3$ upon the charge of sulphur, instead of 3 per cent.). The neighbouring works, burning the same pyrites under identical conditions only allow 5 to 6 per cent. oxygen, and I think this decidedly right.

But if it is established that a certain excess of oxygen, although its presence increases the volume of gas, yet also increases the energy of the action in the chambers, it is, on the other hand, at least as well established that too great an excess of air vastly diminishes the yield and seriously increases the consumption of nitre. We here refer to the account of Olivier and Perret's first trials with pyrites (p. 455).

We may assume that in Germany the minimum and maximum of oxygen in the exit-gases is kept between 4 and 8 per cent. In France it is rather lower, say 3 or 4 per cent.; but in England the higher figure 7 or 8 per cent. seems to be preferred in many places. So far as my experience goes, a medium figure, 5 or 6 per cent. oxygen, would in the majority of cases be the proper one to aim at, but, if anything, I would rather allow a margin a little below than above that figure.

Excessive draught acts in a different way, according to whether the admission of air to the burners is regulated in the proper manner or not. If the action of the excess of draught extends to the burners, they will become too hot; sulphur will be sublimed, especially from brimstone-burners, but even from pyrites-burners, and in the latter scars will be formed. If, however, the excess of draught is *very* great, the burners may, on the contrary, become cooled by the excess of air.

If the admission of air below the burner-grates is regulated so that these do not receive too much air, an excessive draught at the end of the system must produce a diminution of pressure in the chambers; air is aspirated through the tiniest chinks and crevices, and in very bad cases the sides of the chamber may be drawn in.

In both cases "false air" gets into the chamber (which means too much oxygen and inert gases), the chamber-space is badly utilised, and the excess of gases carries away both sulphur dioxide and nitrous gases. If the attempt is made to prevent this by employing more nitre, too much work is put upon the Gay-Lussac tower and more nitre will be lost than in a regular way.

In the case of *insufficient draught* at the end of the system there will be too much pressure in the chambers, as the hot gases continue to come over from the burners; after a short time there will be a deficiency of air in these, which is shown by the analysis of the burner-gas and end-gas; the burners first become too hot, as the cooling effect of the air is missing, and scars are formed, whereupon the burners turn cold, the ore burns incompletely, and the gas gets poor. Generally this is accompanied by blowing out of gas from the burners, which might, of course, also be caused by any kind of stoppage in the gas-flue, but cannot be confounded with this contingency, as in this case the pressure in the chambers is not too great, but the reverse. All this again leads to an excessive consumption of nitre, as the lower oxides of nitrogen do not meet with sufficient oxygen, and even NO may go away as such.

Either cause (as a consequence of the above) leads to a bad yield of sulphuric acid, large consumption of nitre, escape of sulphurous acid into the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

In the case of poor ores, and those the sulphur of which is not readily given off, also in the case of burners admitting too much false air, such as the old Belgian burners, too much air gets into the chambers, and the yield is consequently always very bad. At Oker, for instance, in 1859, from a 50-per-cent. pyrites only 100 instead of 300 per cent. of strong acid was obtained, with a consumption of 14·4 parts of nitre to 100 sulphur (Knocke, in *Wagner's Jahresber.*, 1859, p. 148); and the Belgian Commission states, for the four works examined, the yield = 242, 237, 259, and 238 parts, instead of 306 as required by theory. They were able to detect in the escaping gas 0·38 to 1·26 per cent. of sulphur dioxide, and 11·7 to 17·4 per cent. of free oxygen.

The *regulation of the draught* takes place principally or sometimes even exclusively at the exit end by means of the contrivances described (pp. 747 *et seq.*). It is not practicable to depend for this entirely on the ash-pit holes of the pyrites-burners (p. 433), as these must be regulated to suit each individual burner. It is very important not to overlook that the gas-pipe between the burners and the Glover tower and the chamber may be partially stopped up with deposit. In this case the draught at the burner will be bad, but will be little improved by opening the exit-damper ever so wide, and closing the latter will only draw in air at any chance crevice and injure the chamber-process. This cannot be overlooked if the process is properly controlled by regularly testing the burner-gas and exit-gas; if the latter shows enough or more than enough free oxygen while the burner-gas is blowing out, there must be some intermediate stoppage. The lutes or side-plugs, or still better pressure-gauges (p. 777) fixed in various parts of the set will easily allow of localising that stoppage.

On the contrary, some acid makers prefer working in such a way that there is always *ample* draught from the burners into the first chamber, by employing large and very loosely-packed Glover towers; the burners in this case never blow out, and yet the chambers themselves can be worked right to the end with even outward pressure in lieu of inward draught. But there must then be this drawback that, owing to the loose packing, the denitration in the Glover tower will be hardly perfect. This can be obviated by the following plan, which may be usefully adopted in special cases:—The Glover tower is packed as usual, so as to serve as an efficient denitrator and concentrator. From it the gases are still made to ascend a sufficient height, say 6 or 10 ft., in a wide tube, which then turns (avoiding any sharp bends) sideways and dips down into the roof of the first chamber. Thus a siphon is formed, and as the gases in the second descending limb are cooler than in the part rising upwards from the tower (in extreme cases the air-cooling might even be supplemented in summer by water-cooling), this will cause a suction of the gases from the tower, and thus increase the draught from the burners, without drawing the gas away from the chambers too quickly at the other end. Of course this result is much more easily attained by a fan-blast (p. 753).

Exceptionally, air is admitted behind the burners, usually by means of an injector in the first chamber, which is so constructed as to introduce some air together with the steam (p. 743). This must be done where the burner-gases are too rich, and especially where the first supply of air is purposely kept as low as possible, in order to get hotter gas, as, for instance, in H. Glover's brimstone-burner (p. 403), which is intended to concentrate the acid by heat of the gases.

Some chamber-managers contend that no regulation of the draught need take place at the outlet when this has been done once for all, as the outside atmospheric conditions never vary so much as to interfere with the working of the process. But this opinion is decidedly wrong. In most parts of Central Europe the temperature may vary up to 40° C., or even more, between the extreme heat of summer and the extreme cold of winter. But this means that for every 1000 cub. ft. of air required in the coldest season, nearly 1150 cub. ft. must pass through the apparatus in the hottest season, supposing the barometric pressures to be equal. But these latter as well may vary 30 mm., or even more; so that, for instance, 1000 cub. ft. at 760 mm. pressure represent the same weight of air as 1041 cub. ft. at 730 mm. Combining both (and very frequently low temperatures and high barometric pressure go together, as well as high temperatures and a low barometer), 1000 cub. ft. in winter may be equal in weight to 1200 cub. ft. in summer. It is quite evident that such large differences, and even much smaller ones, as they may occur from day to day *must* be compensated by regulating the outlet of the gases accordingly. Nor must it be overlooked that the pressure of wind affects the quantity of gases passing through a given orifice, and this circumstance sometimes during the year has a very serious effect on the draught, even when the burner-house (as it ought to be) is sheltered against the direct action of gusts on the ash-pits.

The great lack of *quantitative* statements as to the draught necessary in various parts of the chamber-system has been partially remedied by an investigation by Nörrenberg (*Chem. Ind.*, 1899, p. 48; *cf.* also the criticism by Eichhorn, *ibid.*, p. 150, and Nörrenberg's answer, p. 237). The required pressure within the chambers can be attained only by a strong up-draught. To produce this, we should make the difference of level between the burners and the Glover tower as great as possible. The gas inlet-pipe from the burners to the Glover tower should rise straight upwards, and should deliver the gases into the tower at the highest practicable temperature. The temperature of the gases leaving the Glover tower should be very little above that of the main-chamber, and any gas to be carried downwards should be cooled as much as possible. The gas leaving the last chamber may descend pretty low towards the Gay-Lussac, which (of course!) produces all the better draught the greater its height and the wider the outlet. The loss of up-draught from the burners should be lessened by giving the connecting-pipes and flues a sufficiently large section for producing the following velocities (having regard to the greatest possible production with normal burner-gases, to the temperature ordinarily attained at the respective places, and the inequalities of work):—

About 0·5 metre per second in the (clean) burner-flues.
„ 1·0 „ „ „ Glover inlet-pipe.
„ 0·8 to 1 „ „ „ Glover grate.
„ 0·25 to 0·5 „ „ „ Glover packing.
(if possible rather less)
„ 1·0 metre per second „ connecting-pipe leading to the last chamber.

The velocity in the pipe leading to the Gay-Lussac and that in the outlet-pipe of the latter should be such that, on deducting all the losses of pressure up to the Gay-Lussac outlet from the effective up-draught, a pressure of 2 mm. water exists at the Gay-Lussac outlet at ordinary temperatures. This is advisable, in order to facilitate the regulation of the final damper. The section of the Gay-Lussac should be equal to that of the Glover tower, or a little less. It should not be made proportional to the quantity of gas at the respective temperatures, on account of the coke-packing. Changes of velocity, curves (especially such with a small radius), and elbows should be avoided as much as possible. By rounding off the edges in the chamber-exits the loss of pressure can be practically avoided.

Hasenclever (*Chem. Ind.*, 1899, p. 27) found in a special case that a Glover tower with good draught showed a pressure of 2 mm. water at bottom and 5 mm. at top; when the pressure was 2 mm. at bottom and 2·5 mm. at top, the tower was found to be obstructed. But he justly points out that no definite figures for the pressure in the various parts of the chamber-apparatus can be stated as a general rule, and that they must be fixed by experience for every special case.

In *horizontal* ducts the loss of pressure can be deduced from the mere observation of the pressure-gauge, but we shall quote a very important remark made to Hasenclever by Dr Drecker, concerning the complication caused by the *difference of level* through the difference of barometric pressure at different heights of the apparatus, neglect of which makes any observations of pressure by a manometer quite unintelligible. Taking the just-quoted example of a Glover tower, showing 2 mm. water-pressure at bottom and 5 mm. at top, but possessing a height of 9·5 m. (about 31 ft.), the difference of atmospheric pressure between the bottom and the top of the tower at 15° C. and 750 mm. mercurial pressure in the barometer is:—

$$\frac{1.294}{1+\frac{15}{273}} \times \frac{750}{760} \times 9.5 = 11.5 \text{ mm. water.}$$

This we must introduce into our formula, and we thus obtain:

$$11.5 - (5 - 2) = 8.5 \text{ mm.}$$

as the real difference of inward pressure in the tower; that is to say, the pressure within the tower is = 8·5 mm. water higher at the bottom than at the top, and this difference has on the one side to carry the weight of the gaseous column, on the other side to procure the movement of the gases. Taking the specific gravity of the gases = 1·374, and the mean temperature within the tower (350° at bottom, 95° at top) = 222° C., and the outward pressure = 750 mm. mercury, we find:

$$\frac{1.374}{1 + \frac{1}{273} \times 222} \times \frac{750}{760} \times 9.5 = 7.10 \text{ mm. water}$$

or a pressure of 7·10 kl. per square metre. The difference 8·5 − 7·10 = 1·40 indicates the pressure, in terms of millimetres of water-pressure, which causes the ascending movement of the gases.

If we call the difference of weight between a gaseous column and a column of air of equal height its *upward stress* or *buoyancy*, in the present case 11·6 − 7·10 = 4·40, we find the *loss of pressure* between two points in the system to be equal to the observed manometric difference of pressure *plus* the buoyancy; in the present case: observed manometric difference (−3) + buoyancy (+4·40) = 1·40 *loss of pressure in that special Glover tower*, caused by frictional resistance between its bottom and top, etc. If the tower were obstructed by deposits, this loss of pressure would become greater, and we can by similar calculations establish for any given apparatus and by special observations the best conditions to be aimed at, but we should commit a great mistake if we attempted to lay down a general rule for all cases from such special observations.

In this case, as well as in well-nigh every other case in chemical manufacturing, it is entirely premature to apply apparently exact mathematical formulæ as a general guide for actual practice, which Sorel has done by applying to vitriol-chambers Clegg's formulæ for the movement of gases in pipes. The extraordinary complication of the case, caused by the sudden expansion of pipes into the enormously larger section of chambers, by the sharp angles through which the gases must sometimes be conducted, by the changes of temperature, and by the chemical reactions which cause alterations in the volume of the gases and vapours, etc., etc., make the application of any simple formula quite illusory. These formulæ may overawe those who are ignorant of mathematics, especially when they contain the (for such people) mystic symbols of higher mathematics, but I know absolutely of no case in the whole range of manufacturing chemistry where the least practical progress has been made by applying complicated mathematical formulæ to chemical operations. The time for this may come in the (probably somewhat distant) future, when the *elements* necessary for such calculations have been thoroughly studied and placed on a secure *experimental* basis.

Supply of Water (Steam).

The regulation of the steam or water-spray is one of the most important parts of chamber-management, and should always be taken in hand by the responsible foreman or superintendent himself. One of the first conditions for enabling him to do so properly is that the tension of the steam should be kept as nearly equal as possible; and it is hardly necessary to point out how much this task is facilitated by a registering steam-gauge or by automatically regulating steam-valves (pp 713, 725). The round of the chambers should be made two or three times a day; at some works it is even made every other hour. It is one of the advantages of the water-spray system (pp. 728 *et seq.*) that there are hardly any variations of the quantity of water supplied, but other difficulties may occur instead (p. 731).

It must be borne in mind that the Glover tower supplies the first or "leading" chamber of a set with a good deal of the steam required. Hence steam or water-spray must be supplied to this chamber in much smaller quantity than when working without a Glover tower, and the position of the jets is also influenced by this (*cf.* p. 725).

A rough indication of the fact, whether too little or too much steam is present, is sometimes sought in the appearance of the glass jars covering the two lutes of the chambers (p. 701). If these show a white crystalline covering of chamber-crystals, which are proved as such by turning green on moistening them, there is evidently a deficiency of steam. If, on the other hand, the glass jars are dripping wet, there is too much steam in the chamber. This is, of course, only to be taken in conjunction with the other observations to be made by the attendant.

The proper indicator for the admission of steam or water is the *strength of acid made in the chamber*, both as observed in the acid-drips (p. 698) and in the bottom-acid. These two are never identical; the drip-acid is always more or less stronger than the bottom-acid. In long chambers there is a considerable difference between the front and the back part, and such chambers should be provided with two or even more different sets of drips.

Considerable difference of opinion exists as to the *strength of acid* most conducive to a proper working of the vitriol-chambers—that is, to the best yield, the greatest production for a given chamber-space, and the smallest consumption of nitre We may say generally that the chamber-acid is kept much stronger in the majority of English works than in the majority of Continental works. Whilst the former mostly keep the acid in the leading chamber from 120° to 130° and the drips often 5° to 10° higher, the usual practice on the Continent is to keep it at 106° to 110°, or at most 116° Tw. At the Rhenania works the acid runs away from 106° to at most 116° Tw. In America I found from 112° to 116°. Only exceptionally higher strengths (up to 124 Tw.) are met with on the Continent or in America.

It is unnecessary to say that both English and Continental manufacturers firmly believe that they are in the right, the former in making stronger, the latter in making weaker chamber-acid. Both contend that in their, and *only* in their way, the best results are obtained. It is difficult, if not impossible, to arrive at any certain decision on that question from a comparison of the data supplied by various works as to the strength of acid, the yields, the consumption of nitre, the chamber-spaces, and so forth. This difficulty arises both from the complication of the various conditions, which interact upon one another, and from the very frequent inaccuracy and incompleteness of the obtainable figures. It is therefore with all reserve that I proceed to give my own opinion on this question (which differs from that given in the first edition of this work, vol. i. p. 346).

All *theories* of the vitriol-chamber process seem to point to the preference of the *weaker* rather than of the stronger acid. Hurter, in his dynamical theory (*J. Soc. Chem. Ind.*, 1882, p. 10), arrives at the result that the chamber-space is inversely proportional to the quantity of nitrogen compounds present, and to the amount of water present in the gaseous condition; in other words, that, other conditions being equal, the quantity of acid produced within a given chamber-space is larger when weaker acid is made than when strong acid is made. It is true that the evidence given for this in the paper just mentioned from the actual results of a number of chambers is very scanty, and certainly not sufficiently conclusive in itself; this was unavoidable, as only such works were quoted which did not possess Gay-Lussac and Glover towers. But, at all events, no contrary assertion can be based on that evidence.

The theory propounded by myself, and the very similar one of Sorel, both of which will be found at the close of this Chapter, also demand that, other conditions being equal, the sulphuric-acid-forming reaction is promoted by a larger amount of water, up to the limit where an excess of water would produce other, injurious, reactions.

Another point to be considered is this, that it is practically impossible to prevent the loss of some nitre, dissolved in the chamber-acid as nitrosulphuric acid, but that the tendency of the chamber-acid to retain nitre in this form rapidly increases with its strength. Theory would therefore demand keeping the acid weaker in order to lose less nitre. Whether this is so or not in practice can only be proved by bringing together a great many *reliable* data, the difficulty of doing which has been pointed out before. It is a fact that sometimes "pale" chambers are the consequence of giving too little steam (that is, keeping the acid too concentrated), and that this evil can be remedied by turning on full steam for a short time, which causes the chamber to become red again.

The practice of most Continental factories, including several German and Austrian works, at which all the processes are followed up in the laboratory with the greatest care, and which are generally admitted to work with the greatest perfection, is in accordance with the just-quoted theories, and comes to this: that the acid in the leading chamber, that is at the same time that which is withdrawn from the process for use or sale, should not exceed 113°, and is best kept at from 106° to 110° Tw. In this way the best yield and the smallest consumption of nitre are attained.

The usual and practically the only reasonable motive of English manufacturers for making their chamber-acid so much stronger is, of course, this, that they save the expense and trouble of concentrating the acid for use or sale. But there is little or nothing in this in the great majority of cases. For the manufacture of superphosphates, which requires an enormous quantity of sulphuric acid, and for which many acid-works are exclusively employed, the strength of 110° Tw. is quite sufficient. For decomposing salt for sale and for making rectified oil of vitriol, a higher strength is certainly required. But at every works provided with Glover towers (that is, at every properly equipped works, and actually in the great majority of existing factories) there is no difficulty whatever in bringing all the acid up to 140° Tw. without any expense, even when starting from chamber-acid at 110° Tw.; and this is done even without Glover towers (for further concentration in platinum stills) at many works by means of the waste heat of the pyrites-kilns.

Some years ago, P. W. Hofmann (*Ber.*, iii. p. 5), starting from the (erroneous) assumption that sulphurous acid in contact with nitric acid and sulphuric acid of, say, 100° Tw., produces much nitrous oxide, N_2O, proposed to diminish the steam in the first chamber (which in his case was only a "tambour" of 3500 cub. ft. capacity) to such an extent that acid of 140° Tw. should be formed; in this way the acid dissolves much nitre, and is run into the following large chamber, where it gets diluted and gives up the nitre. He asserted that he had thus effected a saving of 1 lb. nitre on 100 lb. of sulphur; but as his original consumption of nitre and the yield are not stated, and as, moreover, his chambers had no Gay-Lussac and Glover towers, that alleged saving cannot convey any proof of the utility of his proposal, upon which a vigorous controversy was carried on in the 21st volume of the *Chem. News* (pp. 132, 164, 189, 200, 224). It was then mostly overlooked that Hofmann's small "tambour" of 3500 cub. ft. capacity had very little in common with an ordinary English leading chamber of more than ten times that capacity. Apart from all other reasons, the undoubtedly much greater wear and tear of the chamber, when worked in the described way, would tell much less with a small "tambour" than with a large chamber. But, for the reasons above stated, Hofmann's process seems wrong in principle, and has not met with any success whatever on the Continent, where it was first tried.

In England later on (since 1889), probably without any reference to Hofmann's proposal of 1867, several works in Lancashire began to employ much stronger acid in the leading chamber, up to 140° Tw. It is, of course, out of the question to lose the nitre dissolved in such strong acid; none of it must be used without first passing through the Glover tower, and as it would become too strong therein, and would be incompletely denitrated, a little water is run through the tower at the same time. At one of the works visited by me it was stated that, with the very low chamber-space of 17 cub. ft., per lb. of sulphur, the excellent yield of 41½ cwt. of 96 per cent. salt-cake was obtained per ton of pyrites, with the very small consumption of 15 lb. nitre per ton of pyrites (=0·67 per cent.). These good results were ascribed, firstly, to an extraordinarily large Gay-Lussac space; secondly, to the above-mentioned procedure, by which an unusually large quantity of nitre was supposed to be kept circulating in the vitriol-chamber. It was not denied that there was more wear and tear of the chambers; but it was believed that this was no more than would be compensated by the saving in the process.

At the time of my visit to the above and a few other works, where the same method was followed, the process had not been sufficiently long in use to enable a correct judgment to be formed as to the yield and the consumption of nitre. Everybody knows that it requires many months to make sure of this, and to avoid being deceived by accidental gains and losses. But even taking it for granted that the above-quoted excellent results were really confirmed in the long run, I am very strongly disposed to place these results rather to the credit of the colossal Gay-Lussac towers existing at that factory, of a width of 14 ft. and a height of 60 ft., than to that of keeping the chamber-acid at the dangerous strength of 140° Tw. It is clear that the large quantity of nitre kept in solution in the strong acid of the leading chamber can contribute but very little to the work of oxidising sulphurous into sulphuric acid; its work can be done only whilst running down the Glover tower. But then the same object can be attained quite as well, while keeping the chamber-acid at a lower strength, by supplying the Glover tower with more nitre, either (once for all) in the shape of nitric acid, or (continuously afterwards) in that of nitrous vitriol from the Gay-Lussac tower; the inert stock of nitre at the bottom of the leading chamber is thus very largely reduced, and the confessedly much greater wear and tear of this chamber and of the Glover tower is thus avoided. From all indications it is also likely that less chamber-space will be required in this than in the former case.

It is difficult to say anything general as to the strength at which the *drips of the first chamber* ought to be kept. At one works we find the drip-acid only 2° or 3°, at others 15° or more above the bottom-acid; at others it is always weaker than the bottom-acid. Everything depends on the position of the drips; but so much is certain, that in the same plant the difference between the strength of the drip-acid and that of the bottom-acid is nearly constant, and that the attendant must manage his chambers accordingly. On the average, the drips, where they are taken from the inside, clear of the chamber-sides, show about 10° Tw. more than the bottom-acid; but this holds good only for the ordinary style of working, not for that described above, where the bottom-acid is kept at 140° Tw.; in this case the drips are not very much or not at all stronger; and where the drips are collected at the chamber-sides they are generally somewhat weaker than the bottom-acid.

We have seen above (p. 311) that the tension of aqueous vapour varies both with the temperature and with the strength of the acid; for instance, at 80° (near the chamber-side), acid of 114° Tw. has exactly the same vapour-tension as, at 95° (only 2½ in. within), acid of 128½° Tw. Sorel observed that the acids collected at various points of the same transverse section of the chamber really showed such differences of strength, and that, therefore, it may be said that they are all at an equilibrium of aqueous-vapour tension. This shows how useless it is to compare the drips of different sets of chambers, unless they are fixed in a precisely similar position to one another.

The strength of acid in the intermediate chambers, between the first and the back chamber, is always below that of the first chamber. The second chamber, in a set of three, has generally about 10° Tw. less than the first; but with acid of 140° Tw. in the first chamber the difference between this and the second may amount to twice as much. In a set of four or more chambers the strengths will naturally diminish more gradually.

The *last or "back" chamber* is kept at very different strengths, according to whether there is a Gay-Lussac tower connected with it or not. In the latter case the acid is never kept above 75°, and sometimes as low as 50° Tw., or even less than that. It is, in fact, difficult to keep the strength higher, as there is so little sulphur dioxide present in this case, and as there must not in the chamber be a large quantity of nitre, in order to avoid losing an enormous proportion of it. Thus there is but little acid made here, and it is correspondingly weak. But such weak acid, even at 75°, causes the formation of much nitric acid, which must act on the chamber-lead and is otherwise injurious. Hence with the old style of working without nitre-recovery apparatus, the last chamber was always a very weak link of the set.

In the presence of a Gay-Lussac tower there is no reason whatever for keeping the last chamber below 90° Tw., or even a few degrees above this. There is no formation of nitric acid to be apprehended in this case, and the gases will be better dried in preparation for the Gay-Lussac tower. The practice of some works to go down as low as 75° or 80° Tw. in the back chamber cannot be at all recommended.

Crowder (*J. Soc. Chem. Ind.*, 1891, p. 301) prefers placing the "drips" in the connecting-pipes between the chambers, and keeps them as nearly as possible at the following strengths:—drip from Glover tower to 1st chamber = 95° to 105°; from 1st to 2nd chamber = 130°; from 2nd to 3rd chamber = 122°; from 3rd to 4th chamber = 105°; from 4th to Gay-Lussac = 85°. If the drip from No. 1 to No. 2 chamber stands lower than 130°, the consumption of nitre is increased. [The drips in the connecting-pipes do not correctly indicate the work done in the chamber, as in consequence of the far greater cooling-action the formation of acid in these places must be abnormally large.]

Sorel gives the following directions for the strength of acid to be observed in a set of three chambers (degrees Baumé):—

	Inside drips.	Side drips.	Acid in chamber-bottom.
1st chamber	57-55° Bé. up to the middle. 56 second half.	51-54° ...	... 54·5-55°
2nd chamber	52-53	42-43° first half. 45-47° 2nd "	... 48-48°·5
3rd chamber	52-53°	45-50°	... 48·0-44°·5

We shall now describe *the injurious results of a wrong supply of water* (as steam or spray) to the chambers.

The first and most obvious result of giving *too much steam* is this, that the acid gets too weak. But this is of less importance than another drawback immediately following. If the lower oxides of nitrogen meet with an excess of oxygen (which is always present in the chambers) *and at the same time with an excess of water*, the following reactions take place:—

$$2NO + 3O + H_2O = 2NO_3H;$$
$$N_2O_3 + 2O + H_2O = 2NO_3H.$$

That is to say, they are converted into nitric acid, which, in the first instance, is a much less efficient carrier of oxygen than nitrous acid, and, secondly, is to a great extent dissolved in the bottom-acid; here it assists the acid-forming process very little, and, moreover, acts upon the lead. So long as the bottom-acid is pretty strong (say, up to 90°), it will not retain the nitric acid for a long time, but again gives it off as lower nitrogen oxides by the action of sulphur dioxide; but if the excessive supply of steam continues, it will soon keep the nitric acid back; and as the process is thereby disturbed, even the steam[1] which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid is thus again increased. If this state of matters has once set in, it is not always easily remedied. Cutting off the steam is not sufficient; much more nitre must be put in as well; and yet the bottom-acid only gradually gets up to its normal strength. In the meantime the yield falls off, the consumption of nitr increases very much, and the action of the nitric acid on th chamber-lead does permanent damage. Thus it is apparen that an excess of steam does very much harm; and great car must be taken lest the strength of the acid should go dow below the proper amount. The chambers soon show when the have too much steam by becoming pale. A pale chamber ofte gets red again in an hour after the supply of steam has bee partially cut off.

An excess of steam has another injurious effect, which ca only be explained in detail when treating of the theory of the chamber-process, viz., the formation of nitrogen protoxide, or even of elementary nitrogen, whilst the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrogen protoxide nor nitrogen can be reoxidised to nitrogen-acids; they escape with the other gases, and thus cause a loss of nitre.

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[1] Whenever here, and in other places, we speak of "steam" in connec tion with the supply of chambers, water in the shape of spray or mist is als meant; it would be tedious to mention this in every instan

We will now consider the opposite case, viz., that *the chambers receive too little steam.* According to the theory of the vitriol-chamber process, to be developed later on, this must deteriorate the conditions for the formation of sulphuric acid, since the substance formed in an intermediate state, viz. nitrososulphuric acid, cannot then be entirely decomposed into sulphuric acid and nitrous acid. It will in this case be either separated in the solid state, as "chamber-crystals," or else it will dissolve in the bottom-acid. In actual practice it rarely happens that the deficiency of water is so great as to lead to the formation of solid chamber-crystals within the chambers; more frequently this happens in the connecting-pipes. But it is all the more general, nay, unavoidable, that some chamber-crystals (commonly called "nitre" in this case) dissolve in the bottom-acid. We shall see later on that a certain quantity of "nitre" *must* be present in properly working chambers; but if there is too little steam, this quantity will be largely increased, both by a deficiency of water in the acid mist floating about, which leaves a large quantity of nitrososulphuric acid undecomposed, and by the excessive concentration of the bottom-acid, which enables it to hold more "nitre" in solution. Thus the nitre will be removed from its proper sphere of action, viz., the atmosphere of the chamber, and SO_2 will escape oxidation. Where the chamber-acid is directly used, without first passing it through the Glover tower, this nitre will be finally lost. All this, of course, happens less easily where the bottom-acid is kept at a lower strength, as is usual on the Continent; there is in this case more time for repairing a temporary deficiency of steam, as indicated by testing the drips and bottom-acids for strength and nitre.

A deficiency of steam also acts in this way, that the acid by becoming too concentrated may to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144° Tw. (and this will very rarely happen, even with faulty managements, there is not much harm done. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam; in the case of smaller chambers (tambours) none at all. But this may be carried too far; and then, in spite of the dark-red appearance of the chambers, there is a bad yield of acid, because the water necessary for its formation is missing, and SO_2 and O go away uncombined. This occurs especially when the chamber shows a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are nothing like so serious as those arising from an excess of steam.

Hurter (*The Manufacture of Sulphuric Acid*, Liverpool, 1882, p. 16) gives the following rules for utilising the indication of the chamber-drips:—

1st. If the strength of the acid in the drips is *correct* but deficient in quantity, the chamber is short of nitre.

2nd. If the strength is *high* and the quantity not far short, the chamber is very rich in nitre; but if the quantity is short, it has too little steam.

3rd. If the strength is *low*, but the quantity full up, the chamber has too much steam. If, on the other hand, the strength is low and the quantity short, the chamber is very poor in nitre.

It is needless to say that the indications afforded by these rules would be sometimes very misleading, the conditions being too complicated, if they were not supplemented by direct observations of the amount of "nitre," the temperature, and the composition of the inlet- and outlet-gases, as shown below.

Stinville (Ger. P. 144084) produces in the lead-chambers a circulation of cooled acid, diluted to such an extent that its steam tension is sufficient to furnish the aqueous vapour required for the process. There are three chambers, *a*, *b*, *c*; the gases pass from the Glover tower into *a*, and leave *c* for the Gay-Lussac tower. The bottom-acid flows from *c* to *b*, from *b* to *a*, and from *a* into a cooler, where it is cooled down by means of a water-coil and also diluted by fresh water; in this state it is pumped back again into the chamber *c*.

Supply of Nitre.

It is quite evident that those ingredients from which sulphuric acid is ultimately formed, viz., sulphur dioxide, atmospheric oxygen, and water, must be supplied to the chambers in proportions varying within very narrow limits only, as any undue excess or deficiency of one of these will cause a corresponding waste. Sulphur dioxide being taken as the given quantity, the proportion of water supplied is kept so that a very nearly constant concentration of the chamber-acid is obtained; and in like manner the supply of air is regulated by the draught in such a way that a certain necessary excess of oxygen, but no more than this, is found in the exit-gas. But the matter is different with that reagent which does not enter into the composition of the ultimate product, and only serves as an intermediary agent for combining SO_2, O, and H_2O, without (in theory) suffering any real change or loss at the end of the process. We now call such an agent a *catalyser* (see later on); this is, of course, the "nitre," by which expression we understand all the compounds of nitrogen which are concerned in the manufacture of sulphuric acid, at whatever stage of oxidation or combination they may exist at a certain moment.

It is almost self-evident that the acid-making process can be made more or less rapid by supplying more or less nitre, and that this finds expression in the greater or smaller space which the process requires. In fact, considerable variations may be made in the supply of nitre, according to whether the chamber-space is to be utilised as fully as possible or not; and up to a certain extent it may be said that the supply of nitre must change in an inverse proportion to the chamber-space present. But certain limits do exist here as well, both in an upper and in a lower direction. If there is too small a supply of nitre, the reactions become too sluggish and very disastrous consequences follow, which cannot be avoided by any amount of chamber-space; and if too much nitre is supplied, the temperature rises too much, the chamber-lead is acted upon, and part of the nitre escapes the process of recovery. We shall refer to this subject in detail later on.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or not. In the latter case care must be taken not to have too much nitre-gas in the last chamber; for everything issuing from it is a total loss. Therefore the last chamber but one is kept strongly yellow or red, in order to promote the acid-forming process, but the last chamber only faintly yellow.

The bottom-acid in that chamber, which is usually kept at 50° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This state of the last chamber is attained by giving it much steam; but it will be seen at once that in this chamber very little work can be done unless a very great loss of nitre is suffered; for only if the latter be present in large quantity, the oxidation of sulphurous acid goes on all through the chamber. Therefore one of these two things must be done: either a large quantity of nitre must be sacrificed in order to utilise the last chamber, or the last chamber is practically used only for recovering part of the nitre; thus actually a third or a fourth of the chamber-space is sacrificed, and so much less sulphur can be burnt in that set. For all that, the last chamber is not merely a costly, but also a very inefficient apparatus for recovering the nitre; even if used as such, very little below 10 per cent., mostly above 10 per cent., of nitre in proportion to the sulphur must be employed in order to get a good yield. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. We thus effect a saving of a fourth, up to a third, in chamber-space, at least one of two-thirds in nitre, and mostly also better yield, because up to the last an excess of nitrous gas is present, and no sulphurous acid can escape oxidation by it. In this way the escape of noxious vapours is also much more completely prevented. The construction of the nitre-recovery apparatus, and everything pertaining thereto, has been described in the 6th Chapter. Here we shall only describe the way of managing the chambers themselves in this case. Supposing the set to consist of three chambers (the reader will easily reduce this to any other proportion by analogy), the first chamber into which, in any case, both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, or cascades, or Glover towers, or steam-columns, will always have an excess of nitre-gas. In spite of this the characteristic colour of nitrogen peroxide will not be perceived in the first chamber, both because the sulphur dioxide, likewise present in excess, constantly reduces most of the NO_2 to colourless nitric oxide, and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognised. In the second chamber the atmosphere is already much clearer; and as also there is very much less sulphur dioxide present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphur dioxide present, that the mixture of gases in the second chamber will only show a more or less reddish-yellow.

In the third chamber, however (in a set of more chambers, in the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There should be very little sulphur dioxide remaining here; and before the gas issues out of the chamber into the Gay-Lussac tower the sulphur dioxide ought to be entirely removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will consist not only of colourless nitric oxide, but also of red nitrogen peroxide. This is proved by the last chamber showing a dark red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas observed in the "sight" of the pipe leading to the absorbing-tower the red or orange colour ought to be quite decided. Within the chamber the red ought to be not quite transparent, but dimmed by a mist of water.

The *colour of a chamber* can be observed by opening the manlids on the top or the clay plugs in its side, but in a much more convenient and accurate way by glass windows put in the sides of the chamber itself (as described, p. 701). As soon as the last chamber turns paler, the cause of this must be sought for. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong; and by comparing the other symptoms, especially the strength and the nitrosity of the drips and bottom-acids, the special cause of the fault must be got at. When the last chamber becomes quite pale, it is certain that a great loss is suffered by sulphur dioxide escaping from it; and the latter, on its way through the Gay-Lussac tower, will even denitrate the nitrous vitriol contained therein, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Everything must therefore be done to avert the turning pale of the last chamber.

Apart from the colour, the gradual diminution of sulphur dioxide and the increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than that by colour that it is not worth while to enter upon it in detail. A chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best Continental works regularly make only two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyse the chamber-gas between as well; nor is this necessary, since its colour gives a sufficient indication for the purpose in question.

As well as testing the *chamber-acid* for its strength, it is of great importance to test it also for its *nitrosity* (percentage of nitrogen acids); and this forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitrososulphuric acid) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially because a number of impurities interfere with the accuracy of the process. In practice, however, a simple and momentarily made *colorimetrical test* with ferrous sulphate is sufficient for the object in question, and we shall now describe this.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen are present. With more nitrogen oxides the ring becomes darker; with still more the whole ferrous sulphate solution assumes a deep brown or black colour. In this case effervescence readily sets in, the liquid getting hot, and the dissolved nitric oxide, with the black colour, being driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes of 5 in. height is once or, preferably, twice a day taken to the chambers, and the tubes filled up to about 4 in. with samples of the drip- and bottom-acids of each chamber; at the same time the strength of each sample is taken by the hydrometer, and written on the stand at the bottom of each tube. The acid-samples are then tested, at any convenient place, by carefully pouring on to each about half an inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths marked below, and taking into account the colour of the chamber-gas observed through the windows, a tolerably good idea of the process going on in the chambers is obtained. This certainly should be completed by an estimation of the sulphur dioxide in the burner-gas and of oxygen in the escape-gas, and also by testing the nitrous vitriol, etc., as we shall see in the next Chapter.

Kolb (*Bull. Soc. Ind. Mulhouse*, 1872, p. 309) gives a few analyses of chamber-acids, confirming what has just been said. They refer to an old-fashioned set without Glover tower and with nitric-acid cascades.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Density . .	1·489	1·417	1·445	1·480	1·488	1·478	1·420	1·457
SO_4H_2 . .	59·1	51·6	54·9	58·1	58·6	58·2	51·4	56·0
N_2O_3 . .	0·023	...	0·04	0·023	0·010	0·02	0·170	0·03
N_2O_5 . .	0·000	...	0·02	0·000	0·000	trace	0·040	0·00
SO_2 . .	...	0·008	...	...	...	...	...	...

a, acid from the first or denitrating tambour where the sulphur dioxide of the burner-gas meets the acid of the last chamber and the Gay-Lussac tower; *b*, the same when the chambers were short of nitre; *c*, acid from the tambour where the fresh nitric acid ran over the "cascade" (excess of nitre); *d*, the same, short of nitre; *e*, acid of the "large chamber"; *f*, acid of the last chamber, normal process; *g*, the same, large excess of nitric acid—liquid green and nitrous; *h*, the same, normal process.

The following rules may be laid down for the *reactions on nitre which the various samples of acid from the chambers and drips ought to show.* Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first or leading-chamber* ought not to show any nitre whatever; if it does so, it is a strong indication that the supply may be shortened. (It must be borne in mind that a slight quantity of nitre, which can be discovered by finer tests, is nearly always present even in the first-chamber acid, but the above-described rough test ought to show none at all or very little.) But first it must be ascertained if, on the other hand, the *drip* of this chamber does not show any nitre; for in this case we must infer that there is *too little steam* in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Mostly this will be confirmed by both drip- and bottom-acid being too strong; and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough; in this case the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the acid of the first chamber smells, on the contrary, of sulphur dioxide; if this is the case to any appreciable extent, there is a deficiency of nitre in that chamber.

The *middle* chambers ought to show already a faint reaction of nitre in the bottom-acid and a stronger one in the drips; the *last* chamber, in any case, a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case as well a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen both if there is too much and if there is too little steam in this chamber: if the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre; if, however, there is too much steam present, that phenomenon will take place which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed and will dissolve in the bottom-acid. Both faults are easily avoided if the last chamber is not kept weaker than 90° nor stronger than 110° Tw.; but sometimes insufficient draught may cause these faults as well. If, on the contrary, the last chamber still appears red, and even the drips still show nitre, but the bottom-acid none, this is an indication which must be instantly met by increasing the supply of nitre; otherwise the chamber itself will soon become pale. If both indications coincide, viz., a pale chamber and a ceasing or weakening of the nitre in the drip, this might still be due to an excess of steam; but rarely will it be so, as anyhow that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Whether the draught is insufficient is most easily tested by estimating the oxygen in the escape-gas; whether it is too large, by estimating the sulphur dioxide in the burner-gas; but in the case of very leaky chambers, which properly ought to have been stopped already, air enters directly into them, as is proved by the oxygen coming out too high in the escape-gas. Where no gas-analyses are made, the formerly mentioned external indications for judging of the draught are taken into account; but these are far more deceptive than gas-analyses. When the draught is not large enough, the nitric oxide does not meet enough oxygen to be oxidised; it is colourless, and, owing to its insolubility in strong vitriol, is altogether lost. This will be recognised by the appearance of red vapours on the gas issuing out of the chimney, where the nitric oxide is oxidised by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. When there is too much air present, the nitrogen acids are carried away mechanically, and the chambers equally lose their colour; at the same time sulphur dioxide goes away, as it has not time to be oxidised.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or entering of air through chinks in the chambers and mechanical carrying away of gas, will frequently *react upon the burners*, since by the insufficient condensation of gas the draught from the burners towards the chambers is diminished. Then all the appearances will take place which are caused by very bad draught in the burners, especially incomplete burning and formation of scars, which, again, weakens the draught. In this case as much nitre as possible must be given, in order to force a better formation of sulphuric acid; and, if necessary, even the burner-charges must be diminished.

But if the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, it is due to want of the latter, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. Undoubtedly several circumstances often act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, instead of N_2O_3, only NO or even SO_2 get into the absorbing-tower, not only will the draught have to be increased, but more nitre will have to be given as well, in order to make up for the loss. Just in the same way, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot entirely retain it), not only will the draught have to be moderated, but more nitre will have to be introduced till everything is in order again.

An *excess of nitre* is detected by the colour of the chambers being too dark, by the strong nitrosity of the acids, and by the fact of the Gay-Lussac acid showing the presence of nitric acid, consequent upon an excess of N_2O_4 in the last chamber.

We thus see that, in nearly every case, when anything goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time; it is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work; and every factory ought to possess facilities for it. If this should not be the case to a sufficient extent, and if without danger to the chambers it is not possible to introduce as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state by easing them in this way.

At some of the best-conducted works it is not thought sufficient to judge of the supply of nitre by the colour of the chambers, the testing of the drips, and so forth, but a system is introduced of constantly checking the amount of nitrous vitriol supplied to the Glover towers, its strength, and the amount of fresh nitre or nitric acid introduced in comparison with the amount of sulphur burnt, in order to keep the quantity of nitre present in the chambers at as constant a figure as possible. As an example of the way in which this account can be kept, I give the following figures, taken from an actual day's work in a well-conducted Continental factory:—

	SET NO. I.	SET NO. II.
Pyrites charged, kl.	10812	10000
Containing sulphur, less quantity left in cinders	4993	4735
Nitrous vitriol used, kl.	10138	10268
Average strength, expressed in nitric acid 36° Bé.	4·86	4·37
Equivalent to acid of 36° Bé., kl.	493	449
Fresh nitric acid supplied, kl.	200	186
Total as nitric acid 36° Bé., kl.	693	635
Equivalent to 96 per cent. nitrate of soda, kl.	520	476
96 per cent. nitrate introduced for each 100 parts of sulphur burnt	10·4	10·1

This quantity, that is, about 10 parts of 96 per cent. nitrate to 100 of sulphur, may be considered a minimum, and only admissible where the chamber-space is very ample—say, about 24 cub. ft. per lb. of sulphur. With less chamber-space, much more nitre, equivalent to 15 or even 20 parts of 96 per cent. nitrate of soda to 100 sulphur burnt per diem, is put through the system. For the "high-pressure style" (v. p. 639, etc., etc.) up to 25 parts of nitre is used; but this involves a correspondingly large nitre-recovery apparatus, without which the waste of nitre would be very serious.

Pemberton (*J. Soc. Chem. Ind.*, 1883, p. 414) quotes a total supply of 15·6 parts of nitre passing through the chambers for every 100 parts of sulphur burnt in the shape of brimstone, with 19·2 cub. ft. per lb. of sulphur. In this case a Gay-Lussac tower was used; whilst in three other cases, where there was no Gay-Lussac, from 8 to 10 parts of nitre were consumed, but with 26·8 to 35·7 cub. ft. of chamber-space. As he gives no details as to yields, his figures possess very little value.

Benker (commun., 1902) employs as a rule 13 parts total $NaNO_3$ to 100 sulphur burnt in twenty-four hours. With very well constructed chambers (*cf.* his views on that point, p. 625) this quantity may be lowered to 9 or 10 parts, but with wider chambers it must be raised to 18 parts $NaNO_3$. This allows with "high-pressure work" to make 8 or 9 kl. acid of 116 Tw. per cb.m. of chamber-space (say, 0·3 to 0·37 lb. H_2SO_4 per cub. ft.). When starting a new set of chambers, the first care is to see that the above quantity of nitre is provided. (*Cf.* also the statements of Davis, p. 640.)

Proposals for Modifying the Ordinary Way of Supplying the Chambers with Nitre.

A proposal made by the Manufacture de Javel (B. P. 1752, of 1882) seems to be worthy of more notice than it has received. The nitre is not to be introduced into the leading chamber only, where the temperature may thereby become excessively high, but to a small extent also into the following chambers, whose temperature is sometimes too low. Even the acid for feeding the Gay-Lussac tower is to contain a little nitre, in which case no SO_2 can escape through the tower.

The United States Chemical Company, Camden, N.Y. (Amer. P. 325262, of 1885), injects nitrous vapours into the last chamber, after having first injected steam, in order to counteract any too strong reduction of the nitrogen-oxides.

Starting from a contrary view, Benker (B. P. 1168, of 1895; *cf.* Kienlen, *Monit. Scient.*, 1895, p. 311) injects SO_2 (in the shape of gases from the front of the first chamber) into the last chamber, in order to remedy the drawback, occurring in the "high-pressure work," that vapours of N_2O_4 are formed which, as he believes, are not sufficiently absorbed in the Gay-Lussac tower. These are to be reduced to N_2O_3 by SO_2. This is evidently the same principle as that involved in Benker's former process (p. 839); the only difference is that he injected the SO_2 immediately in front of the Gay-Lussac tower, and that Benker now sends it into the last chamber. In regular work this process might act injuriously; but in cases where there is an excess of N_2O_4 it may do good. According to a communication from the inventor (1902), this process is not applicable where there is a great distance between the first and the last chamber, in which case the SO_3 contained in the gases aspirated from the first chamber by means of the injector, is changed into H_2SO_4 in the connecting-tube.

The Swiss Société le Nitrogène (Fr. P. 404071) replaces nitric acid in the lead-chamber process by a mixture of nitroso-sulphuric acid and nitric acid, obtained by thoroughly saturating concentrated sulphuric acid, of 75 per cent. SO_3, with nitrous gases diluted with a great extent of air or an indifferent gas.

Temperature of the Vitriol-Chambers.

At every sulphuric-acid works the temperature of the chambers is a subject of constant observation on the part of the attendants, and it is generally understood that the regular and economical working of the process is intimately connected with keeping the temperature at a certain height, different in different parts of the same set of apparatus, and considerably varying in analogous parts of the apparatus at different works but to be kept as nearly as possible equal and constant in the same place. The care with which the observations of temperature are made certainly varies very much. In Germany for many years past *thermometers* have been fixed in several parts of the chambers, generally near the "drips" (p. 698), and their readings are regularly recorded. In France and particularly in England this has been very much less the case; even in large and otherwise very well-managed works chamber-thermometers were frequently not to be found even in recent times, and it was often thought sufficient to test the temperature of the chambers by putting the hand upon the lead. It is hardly necessary to say that the latter plan is decidedly faulty, and the small expense and trouble of applying and using thermometers ought never to be shunned.

This is independent of the question, whether a certain temperature is or is not the theoretically best for the process of sulphuric-acid making, and whether this is the *cause*, or the *effect*, of the economical working of the chambers; for there is no diversity of opinion as to the fact that all causes leading to a faulty process act either directly or indirectly on the temperature of the chambers, and that the observation of the latter is one of the most important guides for judging of the proper working of the acid-making process.

Considerable diversity of opinion exists concerning the *best temperature for the chamber-process*; but there is no doubt as regards some general facts. The temperature of every chamber diminishes from front to back, and naturally even more that of the last chambers compared with the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot that it cannot be touched by hand for any length of time, say 50° to 65° C.: in the absence of any cooling-apparatus, Glover tower, etc., the heat becomes so high that the lead cannot be touched with impunity; but in that case the chamber will not last very long. The second chamber mostly shows on the outside hardly more than blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60° C. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside its temperature varies from 40° to 30°, and below that.

At the Aussig works I noticed in September that the tambour showed 60°; the large chamber in its first part 45°, in its last part 43°; the first back chamber 30°, the last (kept without any steam) 20° C.

At Stolberg (1902) the maximum temperature in the front part of the first chamber was 70 to 80° C. in summer, and 10° or 15° less in winter.

At Oker, in 1891, during the cold season, the first chamber showed 70° in front, 60° in the back; the second chamber, front 50°, back 44°; the third chamber, front 35°, back 25°. During the summer season the temperatures are 10° to 15° higher in the front, 5° to 10° higher in the back part.

At Salindres the leading chamber is kept at an average of 65° in summer, of 55° in winter. This is a refutation to the assertion of Favre (*Monit. Scient.*, 1876, p. 272), according to whom in the south of France the chamber-process is already disturbed at 65°. But it is true that many skilled chamber-managers prefer working the leading chamber as nearly as possible at 50° to 60° only.

Dr Stahl informs me that in a set of three chambers for brimstone, working without a Glover tower, but where part of the heat of the burner-gas was employed for concentrating acid, the temperatures ranged as follows:—

In the first chamber, near the entrance of the gas, from 80° to 90° C., according to the outside temperature.

In the second (main) chamber, in the middle, from 50° to 60° C.

In the third chamber, about 10° C. above the outside temperature in summer, and 20° C. in winter.

The numerous observations communicated by Crowder (*J. Soc. Chem. Ind.*, 1891, p. 301) contain nothing of importance.

The opinion expressed by H. A. Smith, according to whom the best temperature would be nearer 100°, is not based on any valid reasons, and seems to be shared by very few practical men; on the contrary, such high temperatures are universally assumed to be extremely injurious to the chamber-lead, and are carefully avoided. In Europe, 90° or 95° is probably the maximum temperature employed anywhere; but in America I found in one place, where zinc-blende was burned, a temperature of 100°, and it was asserted that this chamber (of course, the first of the series) suffered less than the last; but they had only a few years' experience at that works, so that we cannot accept that statement as conclusive.

The *lower* limit of temperature is by Schwarzenberg put at 40° to 50° C., because otherwise there would not be a sufficient quantity of water remaining in the state of vapour; he asserts that in cool weather a set of chambers is less easily started than in warm weather, and that in winter more nitre is used than in summer. I must contradict this assertion of Schwarzenberg's, both from my own and from many other practical men's experience. Unless the temperature of the chambers sinks so low that ice is formed in them (which may happen in back chambers kept without steam), no excess of nitre is required in winter; on the contrary, at all well-managed factories known to me it is asserted that they regularly require less nitre in winter than in summer, and that the work altogether proceeds better in the cooler season.

We have also seen (p. 730) that it is a mistake to assume that the water exists principally in the state of vapour within the chambers.

A most remarkable case is presented at the Freiberg works, where the cooling of the burner-gas, in order to condense the arsenious acid, is carried on so far that the temperature is equal to that of the outer air, and in winter the gases often enter the chambers at 0°. In spite of this, no inconvenience is felt, and no special contrivances or precautions need be employed; the temperature within the first chamber soon rises to 60° and upwards.

On the other hand, it cannot be doubted that there is at all events an upper limit, beyond which the temperature of the chamber ought not to go. We have seen in Chapter III. (p. 346) that with the same gaseous mixture a comparatively slight rise of temperature, from 70° to 80°, is sufficient to convert the oxidation of NO to N_2O_3 into a reduction of N_2O_3 to NO. Unfortunately we do not yet know the conditions of the process to the extent necessary for *à priori* fixing the upper limit of the temperature of the chambers with any approach to certainty.

In normal circumstances the temperature of the first (leading) chamber will have a direct relation to the quantity of work put upon the system. Whilst with the ordinary allowance of 20 cub. ft. of chamber-space per lb. of sulphur the normal temperature is, as before stated, from 50° to 60°, or at most 65°, it is, with forced work (15 or 12 cub. ft. per lb. of sulphur), 80° at the inlet and rises to 90° or 95° further on; even at the outlet it is still 15° or 20° over the temperature of the ambient air.

Benker (communication, 1902) considers a difference of 10° C. between the inside and outside temperature in the last chamber as a mark of excellent work; 18° or 20° should be never exceeded. He regularly fixes a thermometer on the outside as well as one inside, a course much to be recommended.

The temperature of the chambers depends upon various causes. It is raised by the heat of the burner-gases, by that of the steam introduced, and (in a far greater ratio) by the chemical reactions of the acid-making process; sometimes in hot countries and in unprotected chambers, by the heat of the sun. Part of this heat is withdrawn by the radiation from the thin and quickly conducting leaden walls of the chamber, also by the heat contained in the escaping gas and in the acid drawn off. The loss of heat by radiation will vary according to the season, to the wind, etc., but, of course, much less with chambers enclosed in buildings than with those exposed to the weather. Since for a given time both this influence and the heat brought in by the burner-gases and withdrawn by the exit-gases and the acid manufactured vary but little, the inner temperature will practically be governed by the intensity of the chemical reactions.

The facts now stated prove by themselves that, as I have urged before, *frequent observations of the temperature of the chambers are of great importance for the proper management of the process.* Although the temperatures at the various parts of the apparatus show very great discrepancies at different works, they are almost constant in the same set of chambers, so long as everything is in good working order; and for this reason any considerable rise or fall of the chamber-thermometer, to the extent of say 5° C., is a certain sign that there is some irregularity which should be remedied. This indication is all the more valuable as it is instantly observed without requiring any tests or loss of time, and it is accessible to any ordinary working-man without the aid of a chemist.

One of the most systematic series of observations of the temperatures in different places of a set of chambers was made at the Uetikon works by Lunge and Naef (*Chem. Ind.*, 1884, p. 17). Three readings were made every day, and the following are the averages of a prolonged period, both for (A) moderate duty of chambers (4·4 tons pyrites for 129,000 cub. ft., or 29 cub. ft. per lb. of sulphur), and for (B) intense duty of chambers (6 tons pyrites, or 20·8 cub. ft. per lb. of sulphur). The strength of the acid in the "drips" fixed near the thermometers is also indicated. The extreme variations of the chamber-temperatures, of which only the averages are given here, did not exceed 3° or 4° C. The temperature of the outer air varied far more, viz., 3° to 17° in the fourteen days' working of A, and from 5° to 20° C. in the ten days' working of B; but this did not influence anything except the last chamber. The chambers had all the same width (28 ft. 4 in.) and height (23 ft.); but the leading chamber was 138 ft., the second 65½ ft., and the third 36 ft. long.

	A. Moderate duty.		B. Intense duty.	
	Temp. C.	Strength. Tw.	Temp. C.	Strength. Tw.
Pipe coming from Glover tower	65	...	75	...
Front of leading chamber, near bottom	60	123	69	123
Middle ,, near bottom	60	112½	71	116
,, ,, midway up	61·8	...	73	...
,, ,, near top	64·5	116	76	116
Pipe between first and second chamber	45	119½	57	...
Second chamber near bottom	32	116	41	116
Pipe between second and third chamber	27	...	35	119½
Third chamber	19	116	24	116
Outer air	9	...	12	...

This shows in the first chambers a difference of from 9° to 12° between moderate and intense duty of the chambers. The temperature was very distinctly influenced by the quantity of nitre: with strongly red chambers it was much higher in the front than in the back part; with paler chambers the difference was less, the reaction also going on more equally. At the top of the first chambers the gases were from 4° to 5° hotter than at the bottom, but gas-analysis showed that the gases were not richer in SO_2 and O in the former than in the latter case.

Further experiments were made on the cooling-influence of the radiation from the chamber-walls. The following are the averages of seven days' observations at distances of 10, 4, and 2 in. from the chamber-side, with an average outer temperature of 19°:—

	Distance from chamber-side.		
	10 in.	4 in.	2 in.
Pipe from Glover tower	78°	...	...
Front of leading chamber	72	71	69°
Middle ,, near bottom	74	73	70
,, ,, midway up	76	75	73
,, ,, near top	80	79	77
Second chamber	52	51	50
Third chamber	33	33	32

At an outer temperature of 19°, therefore, the cooling between 2 and 4 in. from the chamber-side averaged only 2°, between 4 and 10 in. only 1°. At lower outside temperatures of course the cooling action would be somewhat stronger. Greater differences were found when the following observations were made in the centre of the chamber by lowering a maximum thermometer by means of a wire through the chamber-top and reading off at the other places as before (the table gives the average of ten observations, at an average outside temperature of 18°):—

Pipe from the Glover tower	73°
Front of leading chamber	69
Middle of ditto, 10 in. from side, bottom	70
,, ,, ,, ,, midway up	72
,, ,, ,, ,, top	76
,, ,, centre of chamber, bottom	75
,, ,, ,, ,, midway up	78
,, ,, ,, ,, top	80
Second chamber	50
Third chamber	29

This shows a difference of 5° between the centre and a place 10 in. from the sides, so that there would be 8° between the centre and the sides. This would seem to indicate that the hot current of gases moves less quickly in the centre than near the sides, and it agrees with the fact that the percentage of SO_2 and O in the centre is greater; that is, that the reaction is less advanced there than near the sides in the same transverse section of the chamber. This would agree both with the theory of Abraham (to be mentioned further on), according to which the gases move in a spiral course from the front to the back end of the chamber, and with that of Sorel, as we shall see in Chapter IX.

The preceding observations clearly show that the chemical reactions produce a rise of the temperatures, as the heat of the gases in the middle of the leading chamber near the top exceeds even that of the gases arriving in the Glover tower, in spite of the cooling action of the air traversing a distance of 70 ft. from the front to the place of observation. This is confirmed by special observations in the fore part of the chamber, where the formation of acid is most energetic:—

	Bottom.	Midway.	Top.
33 ft. from front end	80·5°	83°	81°
66 ,, ,, ,,	75	78	80

Special interest is also afforded by observations made to ascertain the effect of using either *steam* or a *spray of liquid water* for feeding the chambers.

	Steam. (Outer temp. 12°.)	Water-spray. (Outer temp. 24°.)
	°C.	C.
Pipe from Glover tower	69	73
Leading chamber, bottom	71	73
„ „ midway	73	75
„ „ top	76	78
Pipe from first to second chamber	57	68
Second chamber	41	53
Pipe from second to third chamber	36	47
Third chamber	24	31

It is true that in the second case (water-spray) the outer temperature was 12° higher than when using steam; but we have seen above that this influences especially the first chambers but little, and we may thence conclude that there is no sensible difference in temperature between the application of water as steam or that as liquid spray. All this confirms the paramount influence of the chemical reactions.

The following diagrams, Figs. 333 to 337, show the just-mentioned results graphically, the length of the chambers being approximately represented. In Fig. 333 the thick line represents the temperature-curve for a normal duty (20·8 cub. ft. chamber-space), at 12° C. outer temperature; the dotted line for moderate duty (29 cub. ft.), at 9° C. outside; the upper faint line the temperatures observed with a liquid water-spray at 24° outside. Fig. 334 gives the temperatures, obtained in the same series of experiments, as observed in the same transverse section near the bottom, midway, and near the top (the lines have the same meaning as in the preceding figure). Fig. 335 shows the temperature-curves in the longitudinal section of the chambers; the dotted line representing the observations taken at midway height, the thin line the bottom, and the thick line the top. They show very clearly how the temperature is raised by the chemical reactions; near the bottom and at a midway height it begins to fall in the second quarter of the leading chamber, but at the top it keeps up as far as midway. Fig. 336 shows the temperature at different heights in the centre of the first chamber; the dotted line at a distance of 33 ft., the thick line

CHAPTER V

CONSTRUCTION OF THE LEAD CHAMBERS

WE have already seen, pp. 6 *et seq.*, through how many stages the construction of that apparatus has gone in which formerly all sulphuric acid, other than fuming oil of vitriol, was made and up to now is still made for the most part, viz., the *lead chamber*. Also that sulphuric acid is formed by the oxygen of the air being transferred to sulphur dioxide through the intervention of the acids of nitrogen and with the aid of a molecule of water, thus:

$$SO_2 + O + H_2O = SO_4H_2.$$

All the substances entering into the process are in the state of a gas or vapour except the water, which is sometimes introduced as a spray or mist. The reaction takes a certain time, as the nitrogen compounds which serve as carriers of oxygen have to be frequently reduced and reoxidised, and as the gases and liquids are only gradually mixed so intimately that they can actually enter into reaction. There must therefore be a space provided in which large quantities of gas can remain for some time. According to the calculations given on pp. 556 and 558, for each kilogram of sulphur in the state of brimstone 6199, or in the state of pyrites 8145 l. of gas, reduced to 0° and 760 mm. pressure, must enter into reaction; and these figures are a good deal increased by the higher temperature, the steam, etc. In order to harbour such vast quantities of gas, very large spaces must be provided. Since the strongest acids have to be dealt with, both in the liquid and the gaseous form, most materials otherwise used in building are out of the question; and since glass, earthenware, etc., are excluded by the large size of the apparatus, practically only *one* material remains which is sufficiently cheap and suitable for the purpose, viz., *lead.* The disadvantages of this metal, such as its great weight, its softness and lack of rigidity, its low fusing-point, its comparatively high price, cannot outweigh the advantages which none of the base metals share with it for our purpose, viz.:—its great chemical resistance to the acid-gases and liquids; its ductility, which permits rolling it into large sheets; its extraordinary pliability and toughness, in consequence of which it can easily be shaped in every possible way; and, lastly, even its easy fusibility, which permits the edges of two sheets to be so completely united by melting together with a strip of lead, that they form a whole for all practical purposes, and that it is thus possible to make vessels of indefinitely large size and any shape, provided care be taken to support the walls of the vessel on the outside, lest they collapse by their own weight.

A special advantage of lead is this, that even after a number of years, when the chambers have become quite worn out, the greater portion of its value can be recovered by remelting the material; even the mud containing lead can be utilised.

The attempts to make sulphuric-acid chambers from other materials than lead have completely failed. To this class belongs the proposal of Leyland and Deacon (British patents of 10th September and 2nd December 1853) to make them of hard-burnt firebricks, slate, sandstone, basalt, etc., set with a mixture of melted sulphur and sand. *Vulcanised india-rubber* or *gutta percha* are just as useless; Krafft (Wagner's *Jahresber.*, 1859, p. 137) found that gutta percha in an acid-chamber loses six times as much weight as lead, and half as much again of its surface. It would be absolutely impossible to use it, because it softens at the temperature of the chambers, and in that state is even more easily acted upon by the gases. Simon's *zeiodelite* (*Dingl. polyt. J.*, clv. p. 100), a mixture of 19 sulphur with 42 pounded glass, to be employed in slabs of ½ in. thickness, has, no doubt, never been so much as tried for this purpose, no more than the *sheets of glass* proposed by Wilson and others.

General Notes on the Erection of Lead Chambers.

The chambers are always placed at some elevation above the ground-level. At the present day chambers are probably nowhere found placed on the ground itself, or on such low foundations that one cannot at least walk underneath; mostly their bottoms are much higher than this. The first object of this is to give the opportunity of ascertaining whether the chambers are tight. If their bottoms are not easily accessible, large quantities of sulphuric acid may get lost in the ground before this is detected. And this means not merely a loss of the acid, but still more: the foundations are corroded and undermined, and the whole structure may collapse. The expense of building the chambers on pillars, etc., is not thrown away, as the whole space underneath can be used as a warehouse, which in winter time has always a moderately high temperature; or it may even, if high enough, be utilised for the pyrites-kilns, etc., although this course is not to be recommended. In the latter case the chambers should be from 17 to 20 ft. above the ground. At some works, which are pressed for space, even the saltcake-furnaces, ball-furnaces, etc., are built underneath the chambers; but the space below them must then be at least 30 ft. high.

In any case the soil must first be examined to ascertain whether it affords a safe *foundation;* for if the soil settles more in one place than in another, the chamber gets out of plumb and its bottom out of level, which, owing to the acid lying on the latter and to the instability of the chamber-sides, causes great inconvenience. A rocky or pebbly ground is best; next to this, sand or clay; marl or limestone are bad, because sometimes acid will run over accidentally, which acts upon it; and this may happen even with clayey soil. In such cases the whole soil underneath the chambers must be protected by a layer of asphalt.

The pillars upon which the chamber is erected must, of course, go down to the "rock," as in any ordinary building of considerable height. If the accumulation of made ground or loose earth is so deep that it would be too costly to excavate and raise the pillars from below, piles must be driven in, according to well-known building-rules, and the pillars built upon these.

The pillars themselves can be made of brickwork, stone, cast iron, or wood. Sometimes, instead of single pillars, two longitudinal walls are erected, connected by cross joists and interrupted by doors, windows, etc., as shown in the sketch

Fig. 158. Such long walls require much material and make the room underneath the chambers dark, in spite of the windows. They are only suitable where the chambers are placed unusually high in order to build furnaces underneath. Up to a height of about 26 ft. metal pillars seem preferable.

The cheapest pillars are those made of wood or bricks; very rarely they are made of stone—much more frequently of the dearer but much stronger and more durable material, cast iron. If made of *wood*, round or canted balks of at least 10 in. (better 12 in.) thickness must be employed. Mostly fir- or pine-wood is used, especially Scotch fir; but the American pitch-pine or yellow-pine, such as is used for shipbuilding, is preferable (on account of its much greater durability) in spite of its higher price. This applies not merely to the pillars, but even more to the frame of the chamber itself. The pillars must vary in their thickness, mutual distance, and the way in which they are stayed, according to their height and the weight resting upon them (which may be taken at 150 lb. per superficial foot of the total chamber-area, for the lead, timber, and acid, the latter alone in a full chamber amounting to 120 lb. per superficial foot); but for an average height of 10 to 13 ft., which will not often be exceeded with wooden pillars, they ought not to be further apart than 10 to at most 13 ft. from centre to centre. In any case they are put into a stone socket projecting from the ground, lest the bottom of the pillar be damaged by any moisture or acid; the stone has at the top a hollow of ½ to 1 in. depth, into which the foot of the pillar fits exactly; at first a

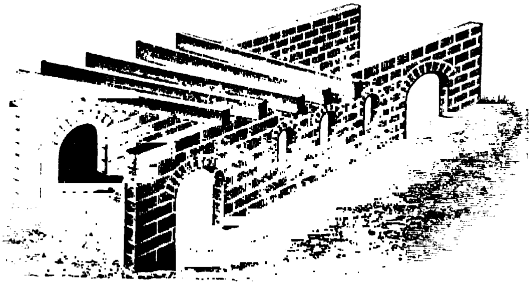

FIG. 158.

little tar is poured into it. Wooden pillars do not last for ever; they are not to be trusted very much, and are rarely found now in larger works, at any rate as principal pillars, except where wood is very cheap.

Frequently *brick pillars* are employed. These also are not often made above 13 ft., at most 15 ft. high. Their horizontal section should be at least 18 in. (better 2 ft.) square. They are made of common bricks, with a mortar very poor in lime.

The brick pillars in many works have been replaced by cast-iron ones, because the former are not very durable, especially at the top, where the beams rest. Even the bricks themselves are rotten by contact with the acid. They stand better if previously soaked in hot tar; but they take the mortar very badly after that. They may also be painted with hot tar afterwards.

On the Continent, where in consequence of the colder winters and hotter summers, the chambers have to be placed in a closed building, the pillars may be built in a piece with the main walls of this building; but it is even then best to keep them separate, as they settle down differently from the main walls.

Chambers 20 ft. and upwards in width are sometimes built with mixed pillars—viz., brick pillars for the two long sides, and wooden pillars for the centre row.

Stone pillars are not often used for acid-chambers. Made of rough stones, they would be extremely clumsy; and hewn stone in most places is too dear. On the other hand, of course, stone pillars of the latter kind are very substantial, and last almost for ever, unless the stone be very soft and rotten.

In the larger works in England *cast-iron* pillars are almost exclusively employed, in spite of their higher cost. These can be made 30 or even 36 feet high; they take very little space, and are almost imperishable if painted from time to time. They can be weighted a good deal more than any other pillars, unless these are made very thick; and they can be used as supports for many other purposes by means of cast-on brackets or even of pieces bolted on subsequently. A brick or stone foundation must be made for them up to the level of the ground or a little higher; the top stone is made with a socket to receive the foot of the pillar, as in the case of wooden ones; or holes are drilled into the stone, corresponding to other holes in the base of the column; and the joint is made by iron cramps, fastened by pouring in melted lead, or in some other way.

The cast-metal columns are now frequently made of an H-shaped section and a little tapering upwards. Fig. 159 will show this more distinctly, together with a bracket on each side for receiving a wooden stay for the timber above. Another cross-shaped section is shown in Fig. 160. These constructions are better adapted for brackets, etc., than round columns. If higher than shown here (15 ft.), they must be correspondingly stronger—for instance, for 20 or 24 ft. height, 12 in. diameter at the base. Such columns can be placed at 20 ft. distance from centre to centre, if the beams resting upon them are strong enough.

Sometimes the columns are made of *wrought iron*, of the section shown in Fig. 161. They are a little dearer than cast-iron columns, but more durable and reliable.

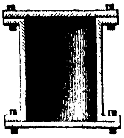

Fig. 161.

The pillars are in most works placed so that they stand directly under the side frame, which has to carry the weight of the chamber sides, and in the English system also the whole weight of the chamber top. This, however, in any case suffices

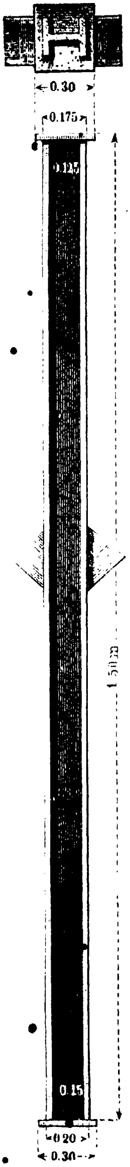

Fig. 159.

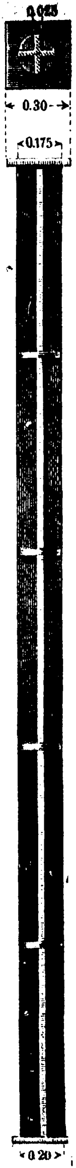

Fig. 160.

only for very narrow chambers; for chambers of ordinary width (from 20 ft. upwards) a centre row of pillars must be added to prevent sagging of the joints. But as the weight of the acid in a full chamber may be up to four times as much as that of the frame and lead combined, it seems more rational to place the pillars more inside, in which case two rows suffice even for a chamber of ordinary width.

Above the pillars there are generally placed *longitudinal sleepers.* If there is a continuous wall in the place of pillars, to cover this with a 2-in. plank will be sufficient; but if there are separate pillars, the sleepers must be strong enough to support the whole structure of the chambers, both wood and lead; and their strength will then depend on the distance between the pillars. With chambers of 20 ft. height, and distances between the pillars of 20 ft. from centre to centre, the longitudinal sleepers should not be less than 12 to 14 in. high, and ought, besides, to be supported by stays, as shown in Fig. 162. With the pillars placed at shorter distances (say 10 or 13 ft.), timber of 9 by 12 in., always on edge, suffices for the longitudinal sleepers. The joints of the beams of which they consist ought to be well connected, as shown in Fig. 162, and should be placed between the pillars, where they are supported from below by the stays. The upper face of the sleepers must be levelled as well as possible from one end of the chambers to the other. Above these the *cross joists* are placed, running from side to side, and made long enough to carry the side frames, and to leave, moreover, a passage round the chambers. For the latter object only every third or fourth joist need project about 5 ft. on each side. The joists are mostly planks on edge.

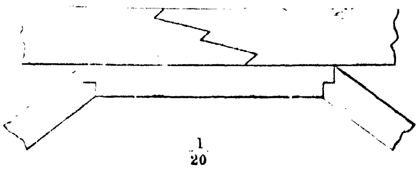

FIG. 162.

If chambers are much less than 20 ft. wide, which is not frequently the case, no central longitudinal sleeper is needed, *and the cross joists should have 9 by 3 in. section and corresponding length.* Wider chambers require a centre row of pillars and sleepers; and in this case, as such long planks are not easy to get, the joists can be made in two lengths, resting on one of the sides and on the central sleeper. The horizontal distance of the floor-joists is usually 12 in. from centre to centre. Some works employ joists of 3 by 11 in. The length of the joists is equal to the width of the chambers *plus* the chamber-frame, *plus* the width of the passage.

The joists are covered with a 1-in. *floor*, laid quite level in all directions. As the flooring-boards might easily warp in course of time from the heat of the chambers, this must be prevented by the well-known methods of carpentry. The edges of the boards are planed so as to form a perfectly smooth floor without any chinks.

Another system of building is more in favour on the Continent. First, from pillar to pillar strong sleepers are laid across the width of the chamber; upon these a large number of longitudinal joists are laid, and the flooring-boards on the top of these, running from one side of the chamber to the other.

Upon the whole the *frame of the chamber* is erected, which serves for supporting the lead. If constructed of *wood*, it consists, for each side of the chamber, of a sole-tree (sill) and a crown-tree (capping), connected by uprights or "standards," and further tied by cross rails or stays. The sole- and crown-trees and uprights are either of square section (say 6 in. square for a chamber up to 20 ft. high) or oblong (say 7 by 3 in.). The sole- and crown-trees lie on the flat side; and the uprights are mortised into them so that their longer side just covers the trees. In the corners the trees project over and are rabbeted into each other. If no cross rails are employed, the uprights are placed 3 ft. 3 in. apart from each other; if they are connected by cross rails, they can be placed 4 ft. apart. The cross rails are 3 in. by 2 in.; they are only partly let into the uprights, in order not to weaken these; and are placed at vertical distances of 4 to 5 ft. from each other. The chamber-lead is kept a little away from the woodwork in order to expose the lead everywhere to the cooling action of the air. If this is not done, the lead is found to be quickly corroded in the parts protected against radiation of heat by the wood; it has even been observed that insects from the wood have bored through it.[1] *It is now usual to shape* the woodwork so as to present the least possible contact with the lead, as shown in Figs. 163 and 164. Almost the same effect is obtained by using round timber for uprights.

The best kind of timber for this purpose, as well as for all others where acids are concerned, is American yellow-pine or pitch-pine; but as this is frequently too expensive, ordinary red-wood is also very much in use. It is beneficial to protect it against the action of the acids by a coating of whitewash, which is at the same time a slight protection against the risk of fire. Another kind of protection from the former, although not from the latter, risk consists in painting the woodwork with coal-tar, or preferably with a sort of tar-varnish, made by dissolving coal-tar pitch in heavy tar-oils, and known as "prepared" or "refined" tar (Lunge's *Coal-Tar and Ammonia*, 4th edition, p. 441). The latter enters better into all the pores of the wood, and on drying does not leave so many crevices; it is altogether preferable to raw coal-tar for painting wood, iron, or brickwork, and is not much dearer.

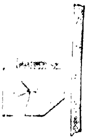

FIG. 163.

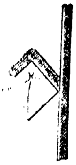

FIG. 164.

The painting of the woodwork is best done twice, and before the lead is put on, so that all parts can be reached by the brush.

Special care must be taken lest any acid gets into the mortise-holes, where the uprights are joined to the sole-trees, etc. No empty space should be left here where any acid could lodge, but all interstices should be filled up with coal-tar pitch or the like. It seems also another good plan to cut out the bottom of the upright, and make it fit on to a corresponding saddle-shaped part of the sole-tree, as shown in Fig. 165. Two small lead pipes drain away any liquid collecting in the low corners, so that no acid can ever lodge there and cause the wood to decay.

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[1] I have described such a case, where the beetles in question belonged to the species *Tetropium luridum* and *Hylotrupes bajolus* (*Z. angew. Chem.*, 1897, p. 527). Observations of the same kind have been made by Hartmann in 1891, by Scheurer-Kestner, by W. B. Hart (*J. Soc. Chem. Ind.*, 1906, p. 456), and others. Messrs Schnorf, of Uetikon, near Zurich, possess a sheet of lead strongly damaged by the attack of a wasp, *Sirex gigas*. Many such wasps still stick in the holes made by them, as they are instantaneously killed when they have succeeded in perforating the lead and thereby come into contact with the chamber-gases.

In France sometimes the bottoms of the uprights are not at all mortised into the sole-tree, but rest flatly upon them, being kept in their places by pressure and friction only.

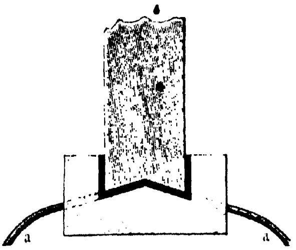

FIG. 165.

Whether cross rails are used or not, in any case there should be diagonal stays, to give more stability to the frame. It is not of much consequence how the stays are put, so long as this is done according to the well-known rules of carpentry.

If, as is usual in England, the chambers are placed in the open air, one side of the frame is made about a foot higher than the other, so that the rain-water and melted snow can run off, and on the lower side a water-spout is arranged so that the rain-water cannot run along the chamber-side down into the acid at the bottom.

At some places the chamber-frames are made of *angle-iron.* This plan has the advantage of presenting an extremely durable and clean erection and of avoiding overheating of the lead in any part. Such frames may be constructed in the following manner. The side-frames consist of thin angle-irons crossing each other at right angles, the uprights 9 ft. 6 in. and the horizontals 7 ft. distant from each other. No iron nails are employed at all; the lead straps are simply bent round the angle-irons. The roof is suspended from angle-irons in exactly the same way. Of course iron frames are more costly than wooden, and must be kept in order by painting from time to time, preferably with coal-tar varnish (p. 591).

R. Moritz (Ger. P. 235800; Amer. P. 981103; Fr. P. 395964) describes a chamber-framing without any uprights between the single chambers. The side-sheets are held by means of straps on rods, extending between angle-irons fastened on the iron roof-frame, and angle-irons fastened to the upper edge of the upstand of the chamber-bottom, which is screwed to the lower cross beams of the building by means of angular stays.

great number of details is given in the specification for this style of frame.

Lead for Chambers.

Now the chamber itself can be erected, and we shall therefore now speak of the *lead* to be employed. For this, sheet-lead as wide as the rolling-mills can supply it, and of convenient length, is used, so as to have as few seams as possible. The usual *thickness* in England is 6 lb. to the superficial foot, sometimes 7 lb., especially for the ends and the top, or for the first chamber of a set.

This thickness is sufficient for a chamber to last upwards of ten years; the bottom lasts longest, because it does not get so hot as the sides and the top, and it is also more protected by the mud of lead sulphate which collects upon it; only in cases of gross neglect (for instance, if nitric acid gets to it) it is quickly worn out, whether the lead be thick or thin. But where *zinc-blende* is used, the *mercury* contained in it may have a different effect, especially since the blende-furnaces are driven at a higher temperature, so that more mercury gets into the chambers. According to information received from Dr Hasenclever in 1902, it has been noticed at Stolberg that the mercury acts most strongly at the lateral parts of the bottom which are less protected by the sulphate-of-lead mud, and where the joint between the side sheet and the bottom sheet causes the double layer of lead to collect acid and mercury between the two sheets. Here sometimes mercury is visible in globules, and that part is worn out in less than three years. Hence at that place the whole bottom is made of stronger lead, rolled extra strong at the part next to the sides, which is, moreover, protected by a covering of acid-proof flags.

In America the usual thickness of lead is only 5 lb. per superficial foot, and even 4-lb. lead is sometimes used (*J. Soc. Chem. Ind.*, 1885, p. 27); but this seems very bad economy indeed, and it can only be done when burning brimstone. In the best American works I have found 6-lb. lead.

On the other hand, at some of the best English works not only is 7-lb. lead used throughout for the chambers, but in the most exposed places, such as the front and back ends of the leading chamber and several feet of the sides adjoining these, 9-lb. is used. Sometimes the side sheets are rolled so that the upper and lower two feet are made stronger than the remainder, because these parts are more quickly worn out. Chambers built in this careful way last upwards of twenty years.

The *quality* of the lead is certainly of great importance. Opinions were formerly not altogether agreed as to the point whether pure or impure lead better resists the action of sulphuric acid; and in the present case it is no doubt not so much this acid as the nitrous compounds to which the attack of the lead is due. Most manufacturers formerly inclined to the belief that "hard lead" is better adapted to vitriol-chambers than "soft lead." A test sometimes performed consists in trying which of several samples of lead in contact with sulphuric acid gives off more hydrogen from a given surface in a given time; but this test is very apt to mislead, and there is really no good test known as yet (cf. *J. Soc. Chem. Ind.*, 1884, p. 230).

This subject has been fully discussed before, pp. 324 *et seq.*, where the conclusion was reached that for vitriol-chambers the *purest* and *softest* lead is the most suitable material. In *Z. angew. Chem.*, 1892, p. 643, I have given the following analyses of lead specially suited for vitriol-chambers:—1. Soft lead of the Mulden lead-works: 0·001 per cent. Cu, 0·044 Bi, 0·0004 Sb, 0·0005 Fe, 0·0004 Sn, 0·0005 Ag, no As. 2. Soft lead from W. Leyendecker & Co., Cologne: 0·0034 Cu, 0·0019 Bi, 0·0029 Sb, trace of Fe, 0·0047 As, 0·00025 Cd, trace of Ni and Co, 0·0010 Ag, 0·0002 Zn, 0·0024 O.

G. E. Davis (*Chemical Engineering*, i. p. 142) quotes the following analyses of "chemical lead" (from what source or by whom made is not stated); the figures indicate milligrams per kilogram (I omit the decimals):—

	A.	B.	C.	D.
Antimony . . .	17	19	64	32
Copper . . .	21	13	14	19
Silver . . .	22	14	39	16
Iron . . .	3	2	12	2
Cadmium . . .	1	1	1	2
Bismuth . . .	4	2	22	4
Zinc . . .	2	1	2	3
Sulphur . . .	1	2	2	1

According to *Eng. and Min. J.*, 8th March 1902 (*J. Soc. Chem. Ind.*, 1902, p. 510), a special brand of lead is designated in Missouri "chemical hard lead," and is sold at 5 cents per 100 lb. above the price of common Missouri lead. It is supposed to contain a little copper and antimony, but no attempt is made to keep the composition within precise limits. Mühlhäuser, in *Z. angew. Chem.*, 1902, p. 758, quotes an analyses of soft chamber-lead from Chicago and St Louis.

Leyendecker (B. P. 2756 of 1901) prepares a special quality of chemical lead by adding either 0·1 to 0·5 per cent. copper or 0·1 to 0·5 per cent. copper and 0·1 to 0·3 per cent. antimony. (Such a patent could hardly be maintained in the face of my researches, quoted *suprà*, pp. 325 *et seq.*, published a long time ago, for the purpose of benefiting chemical manufacturers generally.)

The analysis of such lead, which I have obtained from the Rhenania Chemical Co., as compared with ordinary soft lead, gives the following results :—

	Ordinary soft lead.	Leyendecker's special quality.
Bi per cent. . .	0·00501	0·00605
Cu " . .	0·01787	0·06683
Cd " . .	0·00004	0·00003
As " . .	0	0·00002
Sb " . .	0·00039	0·05025
Fe " . .	0·00089	0·00074
Zn " . .	0·00082	0·00122

Graffweg & Co., of Düsseldorf, also supply a "special quality" of lead, especially recommended for Krell's concentrating apparatus, described on Chapter XX.

We notice, in the "special quality," besides a certain amount of copper and antimony (the latter in such small quantities as not to counterbalance the useful effect of the copper) also an unusually small amount of bismuth, being only 1 : 100 of that present in the "ordinary soft lead." The firm using both had not had a sufficiently long experience with them to judge of any difference in behaviour.

The *Chem. Trade J.*, 1906, xxxviii. p. 91, gives the following analyses of "Good Chemical Lead," in parts per cent.:—

	1.	2.
Bismuth	0·0023	0·0139
Iron	0·0021	0·0021
Antimony	0·0016	0·0011
Copper	0·0008	0·0006
Cadmium	trace	trace
Silver	trace	trace
Zinc	0·0009	0·0005

The quality of the lead used for boiling-down pans will be treated in the chapter describing these pans.

R. E. Robinson (*Chem. Trade J.*, xliii. p. 82) tests "chemical lead" by heating a piece of 1 in. square in a beaker with 500 c.c. concentrated sulphuric acid, and stirring with a thermometer. At a certain point a violent reaction sets up and the metal disappears in about a couple of minutes. With lead suitable for chemical work this takes place at 220° to 240°; with unsuitable lead, at 180° or lower.

All sheet-lead before being used should be "*mangled*," in order to beat out all inequalities and indentations casually produced in transit, etc. For this purpose it is tightly rolled round a wooden roller, about 6 in. thick, and is beaten all the time with a plumber's mallet.

Bakema (*Z. angew. Chem.*, 1904, p. 1446) recommends *coating* the lead, after the erection of the chambers, with black paint, in order to promote the cooling by radiation. The diagram given by him does not show any very strong action in that direction.

Joining the Lead Sheets.—The sheets of lead were, in the infancy of acid-making, joined together by the ordinary *soft solder*, which is very convenient for use, but is soon corroded by the acid. Places soldered thus are also much more brittle than pure lead. So long as the chambers had to be put together in this way, there was occasion for innumerable repairs.

Another plan (which is far better in this respect, but takes much lead, and is only easily applicable for straight seams) is the *rabbet*-joint. The edges of two sheets of lead are turned over in the way shown in Fig. 166, placed one into the other, and beaten down on a smooth surface. Such joints are gas-tight, and have been used here and there in England till within the last few years.

The kind of joint now generally employed is that made by *burning*, employing the lead itself as solder—that is, by melting it with a hydrogen flame fed by compressed air. In this way

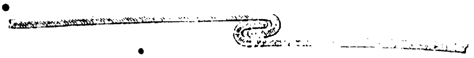

FIG. 166.

the two sheets are joined so tightly, that with good work the joint, being thicker than the sheets, is actually stronger than they are. If the joint is rough and uneven, foreign substances will easily be deposited in the rough parts, by which the lead may be damaged.

This mode of joining was invented by Debassayns de Richemond in 1838. Two apparatus are required for this, whose construction is seen in Figs. 167 and 168. Fig. 167 shows the "plumbers' machine"—that is, the hydrogen apparatus—quite similar to an ordinary laboratory gas-holder, but made of lead, often with a wood casing. The lower vessel, A, contains a lead grating, KL, upon which granulated or scrap zinc is put. The upper vessel contains dilute sulphuric acid.[1]

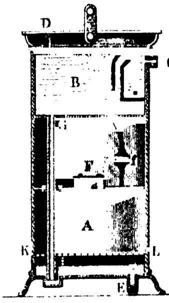

FIG. 167.

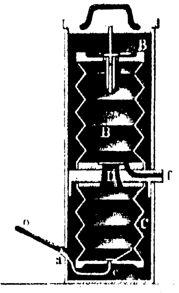

FIG. 168.

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[1] Hydrochloric acid, in the place of sulphuric acid, cannot be employed in the plumbers' machine, as it cannot be left in prolonged contact with lead, and it is also contended that the workmen are injured by the hydrogen made by means of hydrochloric acid.

The connecting-tube with a tap *f* allows the gas to pass ou of the opening C, after it has first been washed in a water vessel. Often there is a plain outlet just above the tap *f* The outlet is connected with a long india-rubber tube, b means of which the gas can be conducted to a distance. Th tube G serves for running sulphuric acid from B to A. It ca only run in if some gas is allowed to escape by opening th tap *f*; and thus a continuous current of gas is obtained. Th openings D, E, and F serve for introducing acid and zinc, an for running off the solution of zinc sulphate.

The second part of the apparatus, which is shown i Fig. 168, is simply a portable smith's bellows of cylindrica shape, the lever of which, *o a c*, a boy works with his foot. Th air is forced through the valve D from C to the closed air-vesse B, and escapes through the opening *f*, likewise connected wit a long elastic tube. The two tubes are united by a blowpipe Fig. 169; and the mixture is ignited. Each limb of the blowpipe is provided with a stopcock, by turning which the plumbe may admit more air or hydrogen at will, and thus can produc a flame of any size, which, however, must never be an oxidisin one.

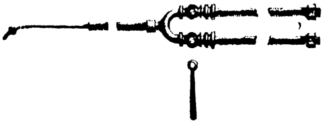


FIG. 169.

The mouthpiece of the blowpipe itself is sometimes connected with the fork-shaped piece by a short elastic tube, t make it more mobile. Besides the ordinary mouthpiece, ending in an aperture of about $\frac{1}{25}$ of an inch diameter, the plumbe also carries another, provided with a small brass shield, to obtai a steady flame in windy weather. The gases unite only immediately before escaping; and thus the flame cannot strik back. By means of this machine a pointed and very ho hydrogen flame is produced, which, at the place where it touche melts the lead immediately down to a certain depth; and th art of burning consists in touching and melting parts of tw sheets *at the same time*, which, on cooling, solidify to a whole.

The *burning* itself is a kind of work requiring much practice, because the plumber must not allow the flame to act a moment too short or too long. If he does the former, the fusion is not perfect and the seam is not tight; if the latter, he burns a hole in the lead. Wherever it is possible, one sheet is laid about 2 in. over the edge of the other, as shown in Fig. 170. The seam is made with the help of a strip of lead, about ⅜ by ¼ in. thick, which the plumber holds in one hand whilst he guides the blowpipe with the other. He works in this way:—He touches with the flame the place *a* (Fig. 170), where the edge of one sheet lies upon the other, so that the surface of the lead (previously scraped clean) just melts, but the back part of the lead does not melt. At the same time he holds the above-mentioned strip in the flame, so that drops fall from it on to the just-melted part of the sheets, and the whole is united into a seam, *b*, all fusing together into one mass. By a slight motion of the wrist the plumber removes the flame for a moment, and the lead, which has only just been melted, at once solidifies; in another second the flame is again directed upon the lead, and a new drop flows partly over the first one; so that at last the whole seam takes the shape shown in Fig. 171.

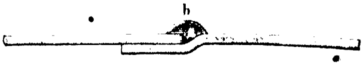


FIG. 170.

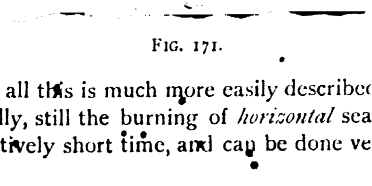


FIG. 171.

Although all this is much more easily described than carried out successfully, still the burning of *horizontal* seams is learned in a comparatively short time, and can be done very quickly by a practised workman. In windy weather it is certainly much more difficult, and in rainy weather it is not possible at all.

The burning of *perpendicular* (upright) joints is much more difficult, and, even in the hands of the most experienced workmen, takes at least three times as long for the same length of seam as horizontal burning, without ever being as strong as the latter. This is easily understood; for the melted lead, which quietly remains lying on a horizontal sheet, in upright burning at once runs down; and this can be prevented only in one way: the lead must be heated exactly up to the melting-point, and the flame instantly removed till the seam has solidified; and the burning must always be done from the bottom upwards, so that to a certain extent the seam will retain the drops of lead. In this case not much use can be made of strips of lead for strengthening the seam.

A practised plumber can burn as much as 10 ft. upright or 25 ft. horizontal joints in an hour; but such figures are only reached in piecework.

Recently the burning of lead has frequently been effected by a pure *oxyhydrogen flame*, both oxygen and hydrogen being applied in the compressed state, contained in steel cylinders. The burning in this way is done much more rapidly. Suitable burners are sold by the Sauerstoff Fabrik, Berlin, O.

Water-gas can be employed for lead-soldering without a blast of air (or oxygen), but its poisonous properties must not be forgotten.

The dangers caused to the workmen by the employment of materials containing *arsenic* in the soldering of lead are discussed by myself on the ground of experiments made by R. Robertson (*Chem. Zeit.*, 1904, p. 1169). He gives the data for calculating the total As_2O_3, corresponding to the arsenic contained in the zinc and sulphuric acid consumed in a day's work of a lead-solderer, at 0·141 g. per diem. It is stated that acute symptoms of poisoning are caused by a quantity of 0·078 g. As_2O_3 per diem being taken up by a man, which cannot possibly be the case if the total arsenious acid getting into the air of the workshop is but 0·141 g. Hence a danger from this source is practically excluded, but more fear might be entertained concerning the arsenic contained in the dust collecting in certain places. This danger should be avoided by frequent renewal of the air and avoidance of collections of dust in the workshop. There should also be a prescription for employing sound rubber tubing for the gas, to avoid leakages. The safest way of removing the AsH_3 is proper washing of the hydrogen, which is effected by a 5 per cent. solution of potassium permanganate, more completely than by cupric sulphate. I greatly recommend electrolytic hydrogen for the burning of lead.

The Griesheim Chemical Co. sells *electrolytic hydrogen*, compressed to 150 atmospheres and sent out in iron bottles, for the purpose of burning lead among others. As pointed out by E. Wiss in *Chem. Ind.*, 1905, pp. 375-378, the use of this compressed hydrogen not merely prevents all and any danger from arsenic, but is also very much cheaper than the evolution from zinc and sulphuric acid. The hydrogen is burned without having recourse to compressed air by means of special burners, supplied by the Griesheim Co.

The way of erecting a lead chamber in England is usually as follows:—The commencement is made with the sides, for which the sheets are made as wide as possible (most lead-rolling mills supply them up to 7 ft. 9 in., some even wider), and so long that they extend 4 in. beyond the height of the chamber, of course taking into account that one side of the chamber is a foot higher than the other. Six inches are reckoned to turn over the crown-tree; but 2 in. are saved at the bottom, because the lead afterwards expands by the heat of the chamber.

Now, on the wooden floor before mentioned a wooden table (the "sheet-board") is constructed, held together at the back by battens, but quite smooth on the upper surface. It has the width of two or three sheets of lead (that is, 15 ft. 6 in., or 23 ft. 3 in.) and the height of the chamber—which, of course, can only be done when (as is generally the case) the chamber is at least as wide as it is high. On this table the sheets of lead are rolled out flat, placed side by side, so that one overlaps the other by 2 in., and burned together; at the same time all the straps (of which we shall speak directly) are burnt to the lead, which can be done because the upper surface will afterwards be the outer one. The upper edge is bent round the sheet-board, so as to hold it fast; and when everything is finished this end is wound up by a set of pulleys, so that the sheet-board is raised together with the sheets of lead, and lies flat against one side *of the chamber-frame.* Now the upper edge of the lead is at once bent over the crown-tree and nailed down, as well as all the straps. For this purpose no cut or wire nails must be used, but wrought-iron nails with broad heads ("plate-nails"), about 1½ in. long, whose heads are protected against the acid by dipping them a few at a time into melted lead. When the lead has been completely fastened to the frame, the sheet-board is lowered down, moved forward its own width, and another piece of the chamber-side made upon it, till in this way the chamber-sides and ends have been finished all round. Only in the corners it is preferable to use single sheets, which form a rounded corner: this is much stronger than a sharp edge. The object of the described process is this, to reduce the upright burning to a minimum. It is much better than the former plan of hoisting up each single sheet, turning its margin over the crown-tree, and unrolling the sheet by its own weight. In this case every single sheet had to be joined to its neighbour by upright burning, and the straps had to be burnt on in an equally inconvenient manner. If at all possible, the seams ought not to be behind the uprights, so as to be better accessible for repairs; and for this reason also it is to be recommended to make the chamber-frame as shown in Figs. 163, 164, or 175, where the uprights do not touch the lead at all.

The *straps of the sides* must be arranged according to the style of the frame. If this consists only of uprights mortised into the crown- and sole-trees, without any cross rails, the straps are made of perpendicular pieces of lead nailed sideways to the uprights with five leaded nails each. The strap ought to be long enough to turn over the edge of the upright, so that two of the nails come to the front (Fig. 172, upper part). Such straps are placed alternately on one and on the other side of the upright, one about every 4 ft. These straps do not allow the chamber-lead to follow the changes of temperature by extension or contraction. This easily leads to deformation of the sides and tearing off of the straps; and it is therefore better to avoid this, which can be done by nailing down only the top strap in the just-described way. Instead of the lower straps, longer pieces of lead are burnt to each side of the upright, which meet on its front, and are there joined by rabbeting (*see* Fig. 172, lower part, and Fig. 173). There are no nails used here, so that the lead walls may move up and down the upright, whilst at the same time they are all the more stiffened by being held fast in two places. This kind of fastening the lead-sheets to the uprights, of course, takes more lead and labour than simple straps. In each case the straps are about 8 in. in depth.

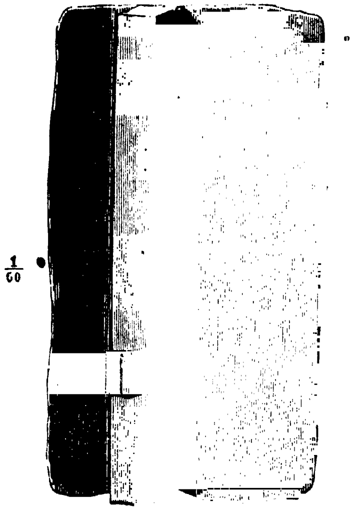


FIG. 172.

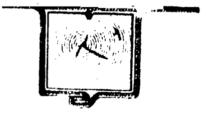


FIG. 173

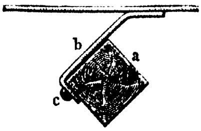


FIG. 174.

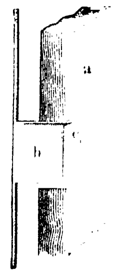


FIG. 175.

The object of keeping the lead clear of the wood, and of giving it scope for expanding, is well attained in the form of strap shown in Figs. 174 and 175. The upright *a* is placed with one of its edges pointing towards the chamber. The strap *b* turns round the edge of *a*, and is fastened to it, not by ordinary nails, but by a broad-headed pin, *c*, which passes through a slit 2 in. in height. This arrangement allows the strap to work up and down as the chamber-side expands and contracts.

If the frame is provided with horizontal cross rails, only a few upright straps are used—sometimes none, only horizontal straps, turned down over the rail, and nailed to it (Fig. 176), two of 6 in. length for each rail. This kind of straps protects the chamber-sides much better against deformation than the upright straps, and carries the weight better upon the frame (this is confirmed by information from Stolberg in 1902); it also permits the lead to be kept further apart from the wood, since the straps may leave about ½ in. (not more) space between the lead and the rails. The diagram shows this.

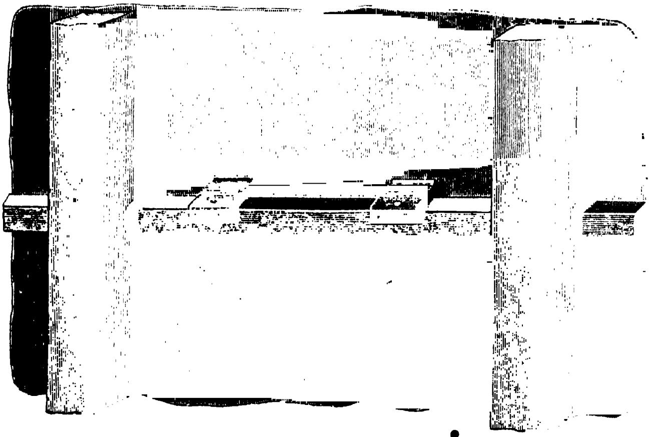


FIG. 176.

The chamber-sides can also (as at the Thann Works) be made of horizontally disposed sheets of lead. The overlap in this case is nailed to the horizontal cross rails in lieu of straps, as shown in Fig. 177; but first the whole height of the chamber-side is finished, the whole is rolled upon a wooden roller, and allowed to unwind itself by its own weight from the top. In this way there is not so much pull upon the seams as if the chamber were made of sheets hanging down by their length, since each sheet is supported just in the place where there would be a pull. This plan, indeed, seems to be worthy of general recommendation; for it saves the lead and labour of all the straps, and supports the chamber very well.

At least as substantial is the plan used at Aussig. There are no side-straps at all; but to each upright of the frame corresponds a strip of lead burnt to the chamber-side along its whole height, the lap being turned outside. This is nailed sideways to the upright. Between this and the lead there is a wooden lath, to increase the contact of air with the chamber-lead as much as possible. Fig. 178 shows this in horizontal section.

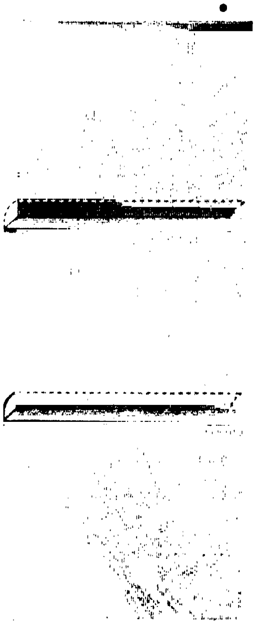


FIG. 177.

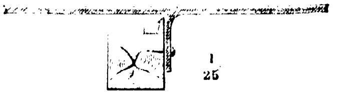


FIG. 178.

Mr Benker ascribes great advantages to his *perforated straps*, shown in Figs. 179 to 181. Fig. 179 is a plan, showing the chamber-side *a*, the uprights *b*, the cross-bars *c*, the small wooden bars *d*, and the straps *e*. The same parts are seen in vertical section in Fig. 180. The chamber-lead is kept 2 or 2½ in. apart from the cross-bars; the perforations of the straps (which may extend the whole width of the cross-bars, as in Fig. 181) cause a strong current of air to rise upwards and cool the lead, without allowing any quantity of dust to accumulate on the straps. This system is especially recommended for chambers which are driven hard for the "high-pressure style" of work (v. *infrà*).

In the first-described case, now generally used in England, at first only about a yard of the seams is burned, and that at the top, so that the chamber can be covered in and the remainder can be done at leisure in bad weather. The next thing, therefore, is the *chamber-top.* For this we need a temporary

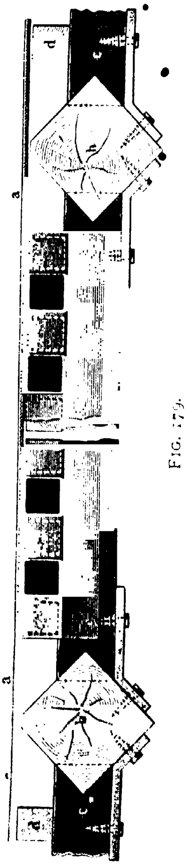


FIG. 179.

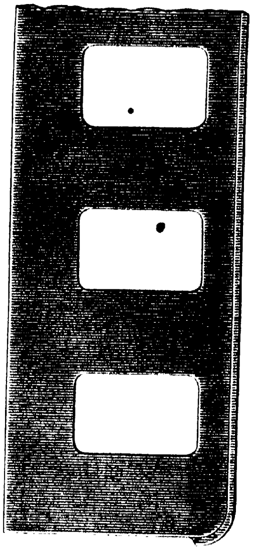


FIG. 181.

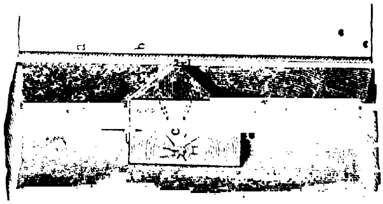


FIG. 180.

scaffolding, movable on wooden rollers, made of high trestles joined together at the top, equal in height and width to the chamber, and in length to at least two (or, better, three) sheets of lead. This scaffold is put together within the chamber itself, its separate parts being got in by bending back one of the side sheets. It is covered on the top with a flooring of boards; and upon this the sheets serving for the chamber-top are flattened out. These are a little wider than the chamber, so that they project 3 in. on each side. Thus they do not project quite as far as the overlap of the side sheets (6 in.), and there remains a joint suitable for burning (Fig. 182, *a*), which is made very strong. Now the sheets themselves are joined by burning, and all the top straps are burnt on. The latter, in England, serve for fixing the chamber-top from above to the top joists carrying it. The latter, for a chamber 20 to 26 ft. wide, are 3 to 4½ in.

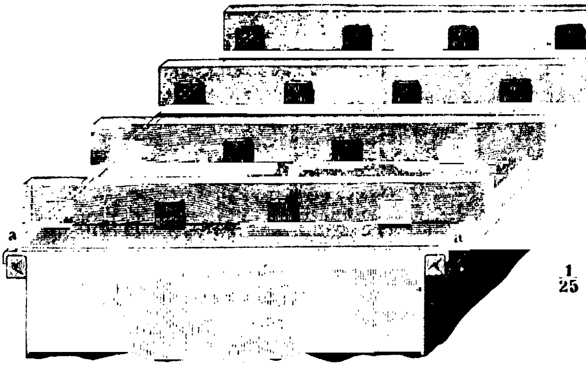


FIG. 182.

thick and 10 to 12 in. high, and are placed at distances of 14 to 18 in. from centre to centre. Their length is at least sufficient to reach to the outside of the crown-trees; it is better if they even project a little beyond, to have a good support. The straps themselves are made 7 in. square, and stand alternately on both sides of the top joists, about 3 ft. apart on each side. At some works there are fewer but longer straps. They are bent up and nailed to the top joists, laid above them on edge, with five leaded nails each. When all this has been done, the top joists, by the help of the straps, carry the lead of the chamber-top, and the joists themselves rest upon the side frames, but separated from them by the overlap of the chamber-sides. The joists should be well clear of the chamber-top (farther than is shown in the figure), so that air can circulate between lead and wood.

The top joists are protected from canting over by a few boards nailed across them, which at the same time serve as a passage on the chamber-top. Where the chambers are roofed in, sometimes longitudinal sleepers are laid on the top, joined to the top joists by iron clamps, and the whole is suspended from the timber of the roof, which must be made strong enough for this purpose; but it should not be overlooked that even in the case of roofed-in chambers it is safer to keep the chamber-top independent of any movement of the roof.

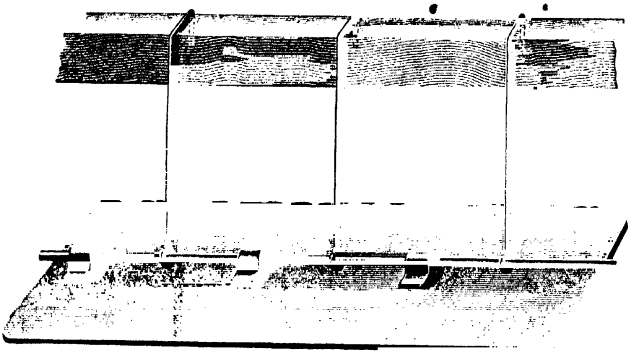


FIG. 183.

Where the chamber is too wide for employing single cross joists, two lengths of these must be joined together and trussed, according to the rules of carpentry; in this case trussed girders may run across the width of the chamber, and the proper joists, to which the top lead is fastened by straps, running parallel with the long sides of the chambers; they are either mortised into the girders, or (which is the stronger plan) they rest in cast-iron shoes bolted to the girders. This, however, is only required for chambers standing in the open air; it is not very convenient, as the side frames have to be weighted very much. Such wide chambers, as we shall see below, have not altogether turned out well.

Quite different from the just-described chamber-tops are those found in many continental works. There are no wooden top joists, but, in the place of these, thin iron rods about ½ in. thick, fastened to the chamber-top by a lead covering burnt on each side to the chamber-lead. These horizontal rods themselves are suspended from the roofing by means of ¼-in. rods placed at short distances from each other. This system cannot be employed for chambers standing in the open air, as it makes the chamber-top dependent upon the beams of the roof; it is shown in Fig. 183.

Another system, which may or may not be connected with the roofing, is the following (Fig. 184):—The chamber-side *a* is carried somewhat higher up, and bends round an iron rod, *b*, ⅞ in. thick, the part coming back over the iron being burnt to the other lead. Here and there holes are left for the passage of the iron hooks *c*, which are bolted to strong joists, *d*. The latter may form part of the roof, or they may be supported quite independently on the crown-tree *e*. The straps *f f* hold up the chamber *g*, and prevent it from sagging; the clear space between *g* and *d* is about 8 in.[3] The object of this arrangement is to prevent all contact between lead and wood even at the top edges of the chambers.

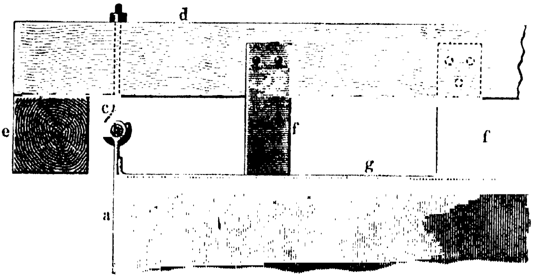


FIG. 184.

At the Griesheim works, in Germany, the following very rational plan of erecting lead chambers is followed:—On a staging of the whole area of the chamber-bottom, but raised over its top, first the chamber-ends are made; over these, without removing the ends, the chamber-sides are made, first one, then the other, and last of all the sheets composing the top are laid down and burnt together. Thus ultimately five layers of lead are lying on the staging one above another. Then the top straps are burnt on and are joined to the top joists, which are put in their respective places. The whole lead-work is now hung from six differential pulleys, and the staging is removed.

As this is done, the ends and sides drop down into their places, and need only be joined in the corners, where they are bent in at an obtuse angle. This mode of procedure causes nearly all the burning to be horizontal, so that the work is done more quickly, cheaply, and substantially.

The *chamber-bottom* is left to the last; and it happens no doubt very rarely (in England probably never) that, according to older prescriptions, the bottom is laid down first and protected by straw and boards while the remainder of the chamber is being made. It is, on the contrary, made last of all, but not always in the same way. In some works the side sheets are burned to it all round, and openings are left in a few places for drawing off the acid, for taking samples, etc. In the majority of works the bottom is independent of the sides, and forms an enormous tank with turned-up sides, into which the chamber-sides hang down, dipping into the bottom-acid, and thus forming a hydraulic joint. This allows the chamber-sides to expand and contract with the temperature, and also makes the bottom-acid accessible from all sides, so that it is generally preferred in spite of the larger expenditure of lead; but a good many works have adopted the first-mentioned plan of making the chamber as a closed box, which saves both lead and the trouble unavoidably connected with the second system. Often the upstand, or "lag," which should not be less than 14 in. high, so as to afford a good deal of room for acid, is made from a narrow sheet of lead of double width, by bending up one half and leaving the other half to form a portion of the chamber-bottom; the latter is then finished by burning it together with other sheets of lead. This is more convenient for the plumber than taking sheets equal in length to the width of the chamber, *plus* the height of the upstand on each side. The latter must not be left loose, because it would be easily deformed out by the side pressure of the acid; to prevent this, a 1-in. board is placed all round the chamber-floor, over the edge of which the upstand is turned round and nailed down. This is shown in Fig. 185. Instead of a solid board, it is preferable to employ merely a number of perpendicular or horizontal rails, which admit the cooling-action of the air upon the lead. At Stolberg the "lag" is made up to 2 ft. 6 in. high, with a correspondingly strong plank to resist the side pressure of the acid.

In some works the bottom is divided into 2, 3, or 4 parts by partitions, reaching up to the whole height of the upstand. The object of this is, not to be obliged to empty the whole chamber in case of repairs; but it is very rarely done, as this arrangement prevents a free circulation of the acid, and as the bottom anyhow mostly suffers less than any other part of the chamber —excepting through gross neglect, by the formation of nitric acid, which ought to be avoided in any case.

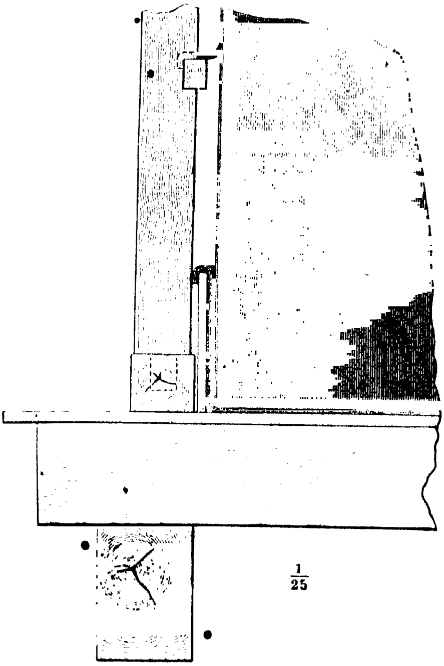


FIG. 185.

Falding (*Min. Ind.*, vii. pp. 679 *et seq.*) gives details of chamber construction which refer to the usual English plan, mostly followed in America as well. Fig. 186 shows part of the chamber-side in elevation. The pillars (posts), *a a*, are of 14 × 14 in. wood; corbels, *b b*, 14 × 14 × 5 in.; stringers, *c*, 14 × 14 in.; joists, *d*, 3 × 15 in., 16 in. centre to centre, 3 × 2 in. herring-bone-strutting *e*; gangway-floor, *e*, with 2 × 12 in. joists. Of the chamber-frame itself, the sill *f* is 6 × 10 in., with a dowel-pin at each post and toe-nail to each intermediate upright. The strong uprights (posts), *g g*, 6 × 6 in., 13 ft. 9 in. from centre to centre; the intermediates, *h h*, 6 × 2 in., 33 in. centres; the bracing, *i i*, 6 × 2 in., with lag-screw to each post and spike to each intermediate. Crown-tree, *k*, 6 × 10 in., with lag-screw at each post

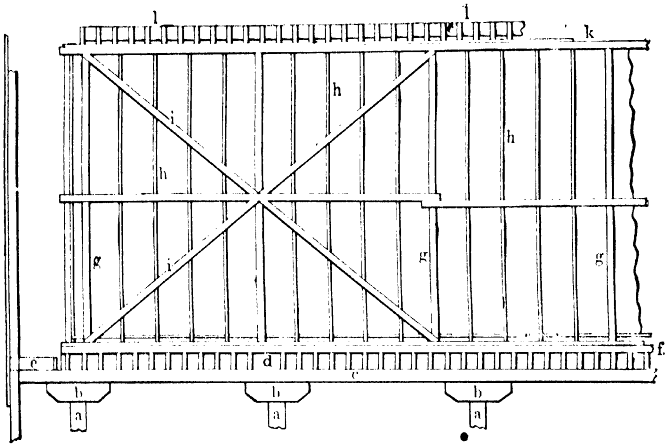
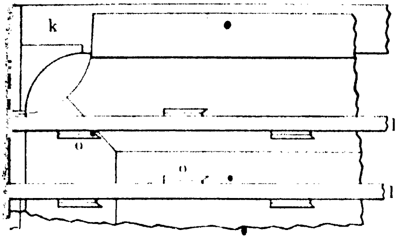


FIG. 186.

and toe-nail to each intermediate upright. Top joists, *l l*, 3 × 15 in., 14 in. centres, with three lines of solid 2 × 12 in. board-bridging. Fig. 187 represents a portion of chamber-ceiling, seen from above, and Fig. 188 the same in sectional elevation on a larger scale, which clearly shows how the chamber-lead *m* at the top is joined to the sides *n*, and turned over the crown *k*, and how the straps *o o* (24 in. centre) suspend the top from joists *l l*. Fig. 189 makes this clearer by a side elevation, and Fig. 190 shows the way the straps are cut from a strip of rolled lead. Fig. 191 gives a plan-section of a chamber-corner, and Fig. 192 a sectional elevation of the lower part of a chamber, showing how the straps *r r* are fastened to the uprights *g*, *h*,

FIG. 187.



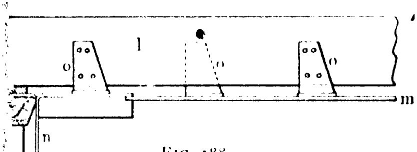
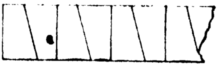


FIG. 188.

FIG. 190.



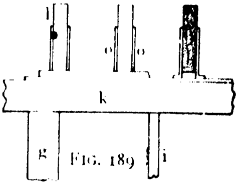
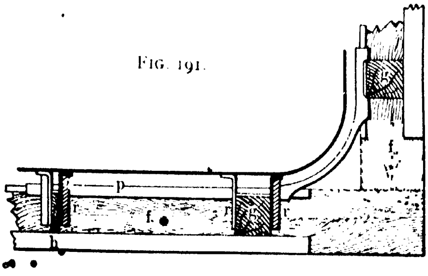


FIG. 189

FIG. 191.



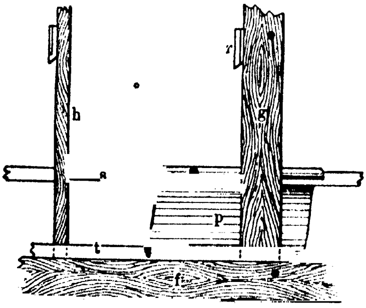
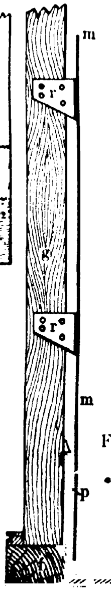


FIG. 193.



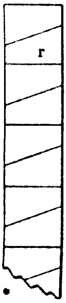


FIG. 194.

FIG. 192.

and how the lead side *m* and the saucer *p* stand off. Lastly, Fig. 193 shows how the upstand *p* of the saucer is turned over ledge *s* (2 × 1 in.) and held at the bottom by another strip, *t* (3 × 2 in.), spoked to the sill.

Special Ways of building Vitriol-Chambers.

As the side-walls of the chambers, in consequence of the variations of temperature, gradually change their form, Petersen and Ising (Ger. P. 218726) make them movable by suspending them on bearings which can slide along the chamber-frame. This allows the changes caused by variations of temperature to take place without any deformation of the lead.

Guttmann (*J. Soc. Chem. Ind.*, 1908, p. 667) describes the way in which a new chamber of 40 ft. height was built. Horizontal wooden beams are suspended by means of iron rods, and can be levelled by adjusting the nuts provided. The whole 40 ft. length of 6-lb. lead (3 mm.) is suspended in two places only in the following manner: An iron rod, ½ in. diameter, is laid horizontally against the lead and held in place by means of straps. A double hook, made of ¼ in. round iron, grips the iron rod at one end, whilst the other end is hung on the wooden beam, where it is hammered flat and nailed down. The hooks are spaced 20 in. apart, so that only about 2 cwt. of lead are supported by each hook. This construction is both simple and cheap. The lead is free to expand, and the hooks being elastic, there is no unequal strain, as is generally the case with straps. The side of the chamber hangs down practically like a curtain, and yields even to wind pressure, while it does not buckle. Such a chamber must be housed, as it would scarcely stand in the open, especially if exposed to strong winds.

René Moritz (B. P. 11123 of 1909; Amer. P. 981103; Fr. P. 395694; Ger. P. 235800) omits the supports of the lead chambers, substituting suspension therefor. His system is described in *Chem. Trade J.*, 1911, vol. xlix. pp. 493 *et seq.* It was first introduced in Northern France by the Soc. anon. des Etabl. Eyken et Leroy, then at other works in France, Belgium, and at the "Union" Chemical Works at Elberfeld. The chambers are supported by a strong skeleton of iron, with a tile roof and outside walls built of bricks laid edgewise, without any windows, light being admitted by glass panels in the roof.

Many ventilating openings are provided, for cooling the hamber-lead. This is suspended by iron rods from the -girders overhead. Along the walls, at distances of 31·5 in., ertical flaps are soldered on; through these light iron rods, ound or flat, pass and are connected above with the pendant upports, while below they are attached by means of spring ooks to the upturned edge of the chamber floor. They give ribbed appearance to the chamber and increase the cooling urface. While imparting a certain amount of rigidity, they ermit of free play for ordinary contraction. Numerous orizontal connections are made with the skeleton framework by means of iron rods. The top of the chamber is constructed on a similar principle. All exposed iron parts are protected from corrosion by a special paint. The chamber top is made in the form of a semicylinder, to prevent the accumulation of dust. The lead floor rests upon an under floor of iron plate, 0·197 in. thick, which is supported by brick or wood or cement columns, 8 ft. high. In all cases the upturned edge of the floor consists of iron plate, bent underneath to a distance of 9·8 in., thus securing a most rapid cooling of that part of the chamber where corrosion is most pronounced. An identical method s used in supporting the lead mantles of the Glover and Gay-Lussac towers. The rounded tops of the chambers produces a nore rapid cooling and closer approach to uniformity of emperature. The cost of construction per unit of cubic chamber space is higher than by the old system, but it is claimed that the rate of production of acid is much larger and he consumption of nitric acid much less, while there is great economy in the matter of repairing or rebuilding the chambers. An illustrated description of the "Moritz" system is given by Barth in *Z. angew. Chem.*, 1909, pp. 1937 *et seq.*; *cf.* also 1911, p. 1446.

Klippert (*Chem. Zeit.*, 1911, p. 649) reports that at Stolzenhagen two chamber systems have been erected according to the "Moritz" system; they cost £2500 more (for an annual production of 12,500 tons acid) than wooden structures, but this extra cost is considered to be compensated by the lessened danger of fire. The same author expresses himself in a similar way in *Z. angew. Chem.*, 1911, pp. 1345 *et seq.*

Buildings for containing Acid-Chambers.—In England, where the winters are not severe, lead chambers are hardly ever placed in a roofed shed, but are only built so that the rain-water can run off as described above. But even then the space between each two chambers must be covered by a light roof, and the whole set must be surrounded by a wooden shed, because a gale might tear the lead off the frames, or even throw down a chamber altogether. These wooden houses have windows or venetian blinds, changed according to the wind. In windy places they are always erected first, as soon as the foundations and the frame are finished, but before the lead has been fastened to the latter, because during the building the incomplete chamber is even more exposed to being thrown down by a gale than after completion.

Thus the chamber tops are exposed in England to the heat of the sun in summer and to the snow in winter; this is possible, because neither of them occurs to an excessive degree. In the less windy places even the chamber sides are sometimes left without protection against the weather, but never so in well-arranged works. (In November 1911, the vitriol-chambers of the Great Lever Chemical Works at Bolton were utterly wrecked by a heavy gale, although protected on one side by a wind-screen.) In the south of France, on the other hand, the chamber tops are always protected against the sun and the rain by a roof; but the sides are generally exposed, which, on account of the heat of the sun there, is certainly very wrong. In the north of France, in Belgium, and in Germany the chambers are always completely enclosed in buildings, usually of a very light construction, and it must be said that this would be decidedly preferable also in the English climate.

Niedenführ recommends placing the chambers on brick pillars, and filling up the spaces between these on the outside with a light wall. The chamber sides are surrounded by a wooden shed and a light roof, employing roofing-felt as a cover for this. He reckons a square foot of such a building, including the chamber-frame, to cost from 3s. to 4s. 6d.

Hartmann and Benker (*Z. angew. Chem.*, 1906, p. 136), in order to keep the chambers as cool as possible, make the framework without horizontal rails, and suspend the chamber top and sides by means of straps hung on iron rods. The passages between the chambers are made of open lattice-work, and a roof-rider on the top produces a constant draught of air along the chamber sides.

Renewal of the Chambers.—The greatest wear and tear is experienced in the first chamber, more especially at the front end, and, as some assert, even more so at the back end and the immediately adjoining parts of the sides. Hence the first (leading) chamber is often made of stronger lead than the others. Besides, it must be noticed that any angular parts of a chamber wear out more quickly than the round or straight portions. The upright corners are therefore always broken or rounded off; but this is not easily managed with the horizontal top corner. Hence, at some works they make the lead stronger in that place (p. 593). The plan of making the chamber roof partly slanting or semi-cylindrical (pp. 615 and 621) may do some good in this respect as well, as this avoids a sharp corner. The "curtain," that is the part dipping in the acid, and alternately subjected to this and to the action of the air, is also liable to quicker wear. There is general agreement on the point that any part of a chamber which gets hotter than the remainder will wear out much more quickly; and this should be guarded against in the construction of the chamber-frame (*suprà*, pp. 590, 592, 603, and 605).

We have constantly laid stress on the fact that the lead should be clear of the woodwork at all possible points, both because it is thus longer preserved by the cooling action of the air, and because it is thus accessible to the plumber. But this condition can, of course, be realised only for the sides and top, not for the bottom. Fortunately the latter suffers least, being protected by the acid itself and by a layer of sulphate of lead. If, however, a leak occurs here after all, it is very awkward to repair. Sometimes this can be done by measuring its distance from the sides, cutting a hole in the chamber top and dropping down a bucketful of plaster of Paris or, preferably, of a mixture of fresh and burnt pyrites-dust, which quickly hardens into a cake and may stop the leak for years. But if this does not succeed, there is nothing left but to stop and empty the chamber, and to enter through the manhole in order to get at the bottom.

A chamber will last very much longer if the frame is substantially made, and the straps are well burnt on and nailed down and numerous enough so that they will not be readily torn off. Should this happen, the mischief must be repaired at once: nowhere does the saying come more true "that a stitch in time saves nine." If the repair is put off too long, the chamber-lead, pulled by its own weight, wrinkles irregularly, and the chamber becomes unfit for work much too soon. Especially those parts of the frame which are most exposed to the action of the acid must be carefully looked after, and, in case of need, repaired at once, before the lead sides dependent upon them have lost their support and have collapsed. This is most necessary at the junctions of connecting-pipes, at the places where the acid is siphoned off, etc. The wind must also be kept off, and any loose pieces in the bratticing round and between the chambers promptly put right; a gale of wind may tear off the straps of a whole chamber side at once, or force the frame to one side (*cf.* p. 616). The gangway round the chambers ought to be wide enough (say 5 ft.) to admit of easy control and repair.

It used to be reckoned that with 6-lb. lead in normal circumstances a chamber would generally last from eight to ten years, but requiring many repairs during the latter years. But since the art of building, and more particularly of *managing*, vitriol-chambers has become better understood, they have been made to continue much longer in use. On the Continent, where they are not (or formerly were not) so much strained as is frequently the case in England, vitriol-chambers generally last much longer than the above term, viz., twenty or even thirty years; but in England as well this is found to be the case at some works where the chambers are built with more regard to durability than to economy in first cost.

There is no doubt whatever that, all other things being equal, a chamber lasts longer in proportion as it is less heated; it is not so much the heat itself, but the intensity of the chemical reactions going on within the chambers, which produces the heat, and moreover the increase of the action of all chemicals by the elevation of temperature brings about the same result. It is only another way of stating this fact, if we say that a chamber lasts all the less time the more nitre is sent into it and the more acid is made in it.

In the case of chambers without a roof the top generally wears out first, after this the parts dipping into the bottom-acid and the ends; the bottom remains good up to the last, unless nitric acid gets to it, which most easily happens in the last chamber, if its strength is allowed to run down too much.

When a chamber requires so much repairing and patching that it does not seem likely to pay, and when, after all, the escape of the gas from the too numerous chinks and rents can no longer be kept down, it is very bad economy not to pull it down at once; for the yield of acid must fall off very much. In this case a temporary connection is made between the two apparatus on either side of it, the acid contained in the chamber is worked down as long as it will run, a hole is cut into its side, and men provided with india-rubber boots are sent in to shovel up the *mud* lying at the bottom into a heap, from which a good deal of acid is still obtained by draining. The mud must now be removed; if the space underneath is free, a receptacle is formed by low banks of clay, a hole is cut in the chamber bottom, and the mud pushed down. If this is not possible, it must be removed in a much more troublesome manner, by thickening it with sawdust and washing with water. In either case it is dried in a reverberatory furnace, sometimes with the addition of a little lime in order to prevent the escape of acid vapours. Notwithstanding this, the operation usually causes a very disagreeable stench, probably owing to arsenic, selenium, etc. The dried mud, principally consisting of lead sulphate, is either smelted for lead in a small cupola heated by coke, or simply sold to the lead-workers.

After taking out the lead-mud, the chamber-lead is detached from the frame, and any better-preserved whole pieces rolled up for use as sheet-lead; the others are melted in an iron pan, the dross is scummed off, and the lead cast in the usual pig-moulds; at the lead-rolling mills this lead is much liked for other chemical purposes (*see* p. 595). Including the pig-lead, the dross, and the lead sulphate, usually nine-tenths or upwards of the original weight of the chamber is recovered; the remainder has disappeared in one shape or another with the acid made.

If the frame has been substantially made, it stands a second, sometimes a third lead chamber, with a few repairs, putting in odd beams, etc. Of course, in case of any doubt, it would be extremely bad economy to run the risk of having to stop a chamber because its frame would not hold out as long as the lead.

Mr G. E. Davis has sent me the following observations:—A set of three chambers (20 × 18 × 120 ft.) had been at work at high pressure for seven years, when the first two chambers were pulled down. They were built of 7-lb. lead; at the end of the time the weight of the top lead was still between 5 and 6 lb., that of the bottom between 2 and 3 lb., the sides were almost *nil*. In the first chamber sulphate of lead equal to 19 tons metallic lead was found, in the second 16 tons metallic lead. The chamber top had not been repaired all this time, the sides had had new lead all round, and the bottom had been repaired in places.

Special observations on the wear and tear of lead chambers have also been made by Burgemeister (*Chem. Zeit.*, 1889, p. 1633). A set of two chambers was observed after twenty-three and three-quarter years, during which time the larger chamber had been at work with brimstone for thirty-two months, then with pyrites (first Westphalian, then Rio Tinto) for one hundred and seventy-eight months, and had been lying idle for seventy-five months. The thickness of the lead was originally 2·57 mm., at the end of the period on an average only 1·88, that is a loss of 0·69 mm. or 26·8 per cent. The part dipping into the bottom-acid was most worn; next to this, the places where the lead was double or where it was protected against cooling by the wooden frame. For this reason it is best to burn the joints outside, because the inner part of the lap-joint is then eaten away first without injuring the joint; if the joint is burned inside, the lap is loose on the outside, and as soon as the inner part is eaten away the chamber must leak. The bottom of the chamber, which is protected by the acid, suffers least. A small chamber which was placed between the Glover tower and the large chamber, and which was kept at a higher temperature (from 65° to 90° C.), had lost in one hundred and twenty working months as much as 17·65 per cent. of the thickness of lead.

Shape of Lead Chambers (*cf.* also p. 614).—The shape of the chambers is usually that of a long box of square or approximately square transverse section. At some places, in order to save lead, the chambers have been made up to 60 ft. wide; but this is not to be recommended on any account. It causes difficulties in constructing the wood frame, and, what is more serious, the yield of acid in such large chambers is not so good as in those of ordinary shape, say between 20 and 30 ft. wide. This is easily understood, as in such very large sections the gases do not get properly mixed, and there are too few surfaces offered for contact and cooling (*cf.* Chapter VII.).

For the purpose of saving lead, the chambers belonging to the different works of the Rhenania Chemical Company are constructed in the way illustrated in Fig. 195—that is, with the top corners cut off, to suit the slope of the roof. This admits of putting the largest possible height of chamber into a roofed building; and Mr Hasenclever also contends that the "dead corners" of square-sectioned chambers are thereby avoided. There is also less wear and tear than in the sharp corners of chambers of the ordinary square section (*cf.* p. 615).

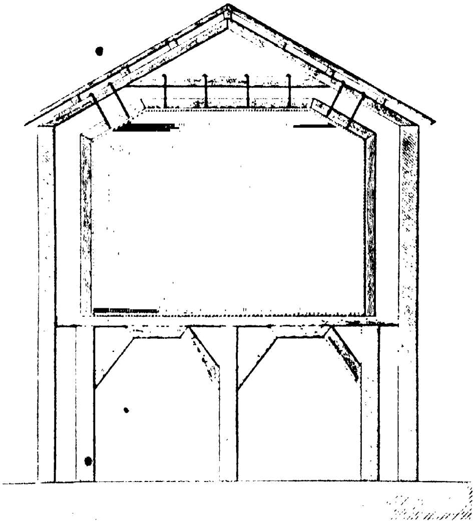


FIG. 195.

The usual width of vitriol-chambers is rarely below 20 or above 30 ft.; their height varies from 16 to 25 ft., or exceptionally a few feet more. Their length (always speaking of the principal chambers, not of the small chambers or "tambours" arranged before and behind these in the French system) is rarely below 100 ft., but may attain 200 or even 300 ft.

H. A. Smith, in a pamphlet on the Chemistry of Sulphuric-acid Manufacture (1873), endeavoured to prove that the upper space of the vitriol-chambers did no work at all, and that chambers of 5, 6, or at most 8 ft. in height would be most suitable. His experiments (described and refuted in detail in our first edition, pp. 285 *et seq.*) were decidedly inconclusive, and a practical test of his theory at the Oker works led to its entire rejection.

In direct contradiction to the theory of Smith is the success obtained by Falding's chambers, to be described later on, which have the same horizontal dimensions as hitherto usual, but are very much higher.

E. and T. Delplace (B. P. 5058, 1890) describe an *annular* chamber, in which the gaseous current is continually changing its direction, owing to that shape. Siphon-shaped tubes placed on each side of the chamber produce a circulation and mixture of the gases. These chambers occupy less space than the usual form, and are stated to produce up to 6 kg. acid of 52° Bé. (= 3·7 kg. H_2SO_4) per cubic metre = 1 lb. sulphur to 13·2 cub. ft. per twenty-four hours. A few sets of this kind have been erected in France and England. According to the *28th Alkali Report*, p. 55, the shape of chamber actually built differs a good deal from that described in the patent. According to information received from manufacturers, the production from these chambers per cubic foot does not exceed those of ordinary chambers.

Th. Meyer's tangential chambers (B. P. 18376, 1898) are also devised as a means for inducing a better mixture of the chamber-gases. The chambers should have a circular or polygonal section, and the gas inlet-pipes be placed tangentially on the upper part of their sides, the outlet-pipes in the centre of the bottom.[1] This imparts a spiral motion to the gases, rapid at the circumference, slower towards the centre, and thus causes them to travel through a greater distance and to get much better mixed than in ordinary chambers. The inventor gives more details concerning his system in *Chem. Zeit.*, 1899, p. 296; *Z. angew. Chem.*, 1899, p. 656; and *ibid.*, 1900, p. 739. His system has been carried out at the Norddeutsche Chemische

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[1] The patent specification speaks of the *ceiling*, but in practice the gas-exit is placed in the centre of the chamber *bottom*.

Fabrik, Harburg, and at the Chemische Düngerfabrik, Rendsburg. The chambers are 10 m. in diameter and 8 m high, in a set of three, with Glover and Gay-Lussac towers. The draught is very good, the yield from 92·5 to 95·2 of the theory (291 H_2SO_4 per 100 S burned); per cubic metre the production is from 3·66 to 3·87 kg. H_2SO_4, with a consumption of 1·34 to 1·44 nitric acid 36° Bé. (= 1·0 to 1·07 nitrate of soda) for 100 H_2SO_4, or, say 3 $NaNO_3$ to 100 S burned.

Hess (*Z. angew. Chem.*, 1905, p. 376) produced in such chambers in January 6·2 kg., in August 5 kg. acid of 50° Bé.; for 100 kg. of such acid he required in January 0·43, in August 0·64 kg. nitric acid of 36° Bé.

[This production is good, but still inferior, not merely to "high-pressure work" with ordinary chambers, but also to that of some of the German works, *cf.* p. 640.]

Later on (*Z. angew. Chem.*, 1900, p. 742) Meyer improved his chambers by arranging in the first (and hottest) chamber a *cooling system*, consisting of forty-three lead pipes, 2 to 2½ in. wide, suspended in water-lutes from the chamber top all round the circumference and reaching 8 to 10 ft. down into the chamber. They are closed at both ends; through their tops enter thin lead pipes, reaching nearly to the bottom of the larger pipes, for introducing the cooling-water, as shown in Fig. 196. The whole offers a cooling-surface of 23 sq. m. (= 250 sq. ft.), *i.e.* 7 per cent. of the heat-radiating surface of the chamber sides and ceiling. The water, of which 8½ tons is used per day, issues at a temperature of 67° C. The heat evolved by the process of converting SO_2, O, and H_2O into H_2SO_4, as far as it goes on in that chamber, is calculated = 2½ millions metrical heat-units per twenty-four hours, of which 500,000 are removed by the cooling-water = 20 per cent. This is not shown by the chamber thermometers, as the loss of heat is made up by that newly generated by the chemical process, but it is manifested by the increased production of sulphuric acid (according to the theories of Lunge and Sorel, *cf.* later on). The pipes last a long time, and can be immediately renewed by taking them out of the hydraulic seals. The hot water is used for feeding the steam boilers.

In *Z. angew. Chem.*, 1902, pp. 151 *et seq.*, I stated that the advantages to be realised by Meyer's proposals by his own showing are not very considerable. It is very doubtful whether or equal weights of lead his tangential chambers produce any more than even moderately well-managed ordinary chambers.

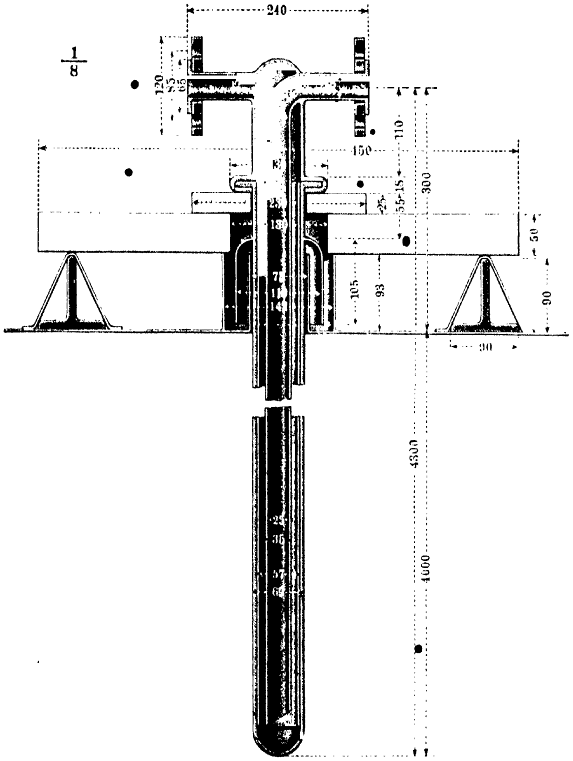


FIG. 196.

This also comes out in the comparisons made by Falding (see below).

Th. Meyer (Ger. P. 186164) later on patented the following improvement of his "tangential chambers." Two or more tangential pipes are placed in various places of the chamber walls, with a section reduced in proportion to the artificial increase of the velocity of the gases produced mechanically (*Fischer's Jahresber.*, 1907, p. 331). Another improvement by the same inventor and described in Ger. P. 326792 is made for the purpose of dealing with the fact that a stagnation of the gases takes place round the exit-pipe at bottom of the chamber. This is now remedied by providing a special outlet-pipe at that place and reintroducing the gases tangentially into the chamber.

In another paper (*Z. angew. Chem.*, 1901, p. 1245), Meyer acknowledges the "Lunge towers" as the best solution of the problem of bringing the *misty* particles floating in the chamber to act upon each other, and he advises to combine such intermediate towers with his "tangential" chambers.

Th. Meyer fully discusses the matter in a pamphlet, *Das Tangential-Kammersystem*, published at Offenbach in 1904, and reviewed in *Z. angew. Chem.*, 1904, p. 477.

According to Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1332), Meyer's circular chambers are a great success. He had satisfied himself that they came up to the guarantee given by Meyer, viz., a maximum of 11·6 cub. ft. of chamber space per pound of sulphur charged with a maximum consumption of 2·7 lb. of nitre per 100 lb. of sulphur. Meyer himself (*Z. angew. Chem.*, 1904, p. 926) and W. Hess (*Z. angew. Chem.*, 1905, p. 376) defend Meyer's system against objections made to it by Hartmann and Benker (*ibid.*, 1904, p. 554).

Beskow (*ibid.*, 1908, pp. 2312-2315) experimentally investigated the way in which the gases travel in Meyer's tangential chambers; he found that in fact the tangential movement prevails in the greatest part of the chamber, both in the upper and the lower part of it, nearly up the centre, whilst in circular chambers of the same size, into which the gases were conducted axially, no definite direction of the movement of the gases could be recognised.

According to Nemes (*Z. angew. Chem.*, 1911, p. 392), up to 1911, thirty-nine factories had been erected on Meyer's tangential system. The cost of plant is rather high, on account of the employment of iron frames, but there are compensating advantages.

Benker, according to direct communications received from him in 1902, employed only narrow chambers, say 18 to 20 ft. wide, and from 25 to 33 ft. high. Such chambers are, in the first instance, better adapted for water-spraying, but they also afford a better mixture of the gases, especially if the sides are cooled, by employing an open bratticing for the side passages (2½ in. laths with 1½ in. clear spaces) and a roof-rider. The cold gases descending along the sides must rise again in the centre; but in the case of very wide chambers a dead space remains where the velocity is very slight, and where the mist of nitrous vitriol sinks down without acting on the gaseous constituents. This cannot produce "high-pressure work" (cf. *infrà*, p. 639). Benker objects to Meyer's tangential chambers (p. 624) that there is no question of tangential action, that in the centre of these circular chambers gases of very different concentrations get mixed up, and that they would be too expensive if the only proper way was followed, viz., building many small circular chambers in a set. We shall later on, when describing the system of water-spraying, give a complete diagram of Benker's chambers.

Grosse-Leege (Ger. P. 162218) describes a circular chamber with tangential introduction of the gases, narrowed towards the exit-pipe for the gases, which is arranged sideways, so that the gases must travel all along the walls of the chamber. Steam-injectors are arranged in such manner that they send out a steam-jet tangentially in the direction of the gaseous current. By means of a spout, surrounding the top of the chamber, with perforated bottom, cooling-water may be run down the outer surface of the chamber (*Z. angew. Chem.*, 1905, p. 1909).

Olga Niedenführ (Ger. P. 189834) describes a circular chamber, with spirally running solid or perforated inner diaphragms, which force the gases to take a similar course.

Fromont (Ger. P. 191723) employs a circular chamber with corrugated sides and inner diaphragms (B. P. 4861 of 1907; Fr. P. 375117).

Fels (Ger. P. 228696) employs as acid-chambers drums, in which fans with smooth or perforated wings produce an energetic mixture of the gases, while nitrous vitriol runs over the bottom in the opposite direction.

Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1332) states that it had become usual in England to prefer smaller chambers to very long ones, and to make their height greater than the width.

Lüttgen (Ger. P. 244402) shapes both top and bottom of the chambers semicylindrically or polygonally, and provides the bottom with holes so that it is kept free from acid. The gases enter the chamber tangentially, and leave it in the same way or centrally, but always opposite to the entrance. Thus they travel in a helicoidal way, and in the end leave the chamber tangentially.

Combination of Chambers to Sets.

Sometimes the whole working-space is contained in one chamber. Scheurer-Kestner (Wurtz, *Dict.*, iii., p. 147) mentions a single chamber of 142,000 cub. ft. capacity, and quotes the experience of different works, according to which it is quite unnecessary to divide the set into several chambers. More frequently, however, several chambers are combined to form a set, which, to begin with, affords this advantage—that for repairs it is not necessary to stop the whole set.

A great diversity of opinion exists as to how the single chambers are to be combined to form sets. Among the hundreds of vitriol-works very few will be exactly alike in this respect; and frequently even in the same works different combinations are found. We may, however, consider it as established that it is almost indifferent in which way the chambers are combined, if they are, in the first instance, properly built (that is, not too high or too wide); and if, secondly, they possess a certain cubic capacity for the quantity of sulphur or pyrites to be consumed. Within these limits those combinations are best which require least lead, and which are laid out so as to afford the greatest facility for supervision. Of course there is also an extreme limit to the capacity of the whole set; but opinions differ upon this point also. At some works a set consists of nine or eleven chambers of 35,000 cub. ft. each; at others, equally large, it is limited to three chambers of 42,500 cub. ft. each, etc. Thus at Hebburn-on-Tyne at the time of my last visit, several sets of three chambers each were employed, each chamber 20 ft. wide, 125 ft. long, 17 ft. high on one side, 18 ft. on the other; each set serves for eighteen burners, burning 7 cwt. daily. At Gateshead there were several sets of three large chambers, each so arranged that two of them communicate separately with a set of kilns ("working-chambers"), and both of them were connected with the third chamber; the whole set had a capacity of about 200,000 cub. ft. More usually the gas passes through all three chambers in succession. Very often four chambers are combined, each of them about 20 × 20 × 130 ft.—or five chambers, two of them working-chambers, thus, $\left.\begin{matrix}1-3\\2-4\end{matrix}\right\rangle 5$,—or even six chambers, thus, $\left.\begin{matrix}1-3\\2-4\end{matrix}\right\rangle 5-6$.

In America (*Z. angew. Chem.*, 1894, p. 133) I found at one place a set of twelve chambers of equal size, each 24 ft. long, which, it was asserted, combined very good yield with small consumption of nitre. At another place they had three chambers, 60, 50, and 40 ft. in length, with plate-columns between.

The chamber-set described by Hasenclever (*Chem. Ind.*, 1899, p. 26) consists of two very large and two small back chambers of a total capacity of 7250 cb.m. = 267,000 cub. ft. He mentions the existence of sets comprising 12,000 cb.m. = 420,000 cub. ft., which is decidedly far too much.

At one of the most modern German works I found sets consisting of three chambers, all of them 10 m. wide and 7 m. high; the first had a length of 41, the second of 31, the third of 10 m. They produce 2·8 kg. H_2SO_4 per cb.m. (equal to about 18 cub. ft. chamber-space per pound of sulphur burnt in twenty-four hours).

The Rhenania Chemical Co. prefers throughout sets of two equally large chambers, followed by two small back chambers (1902).

In France it is usual to combine three chambers in a set, exceptionally four or five. The total capacity of a set hardly ever exceeds 6000 cb.m. (= 210,000 cub. ft.).

According to *Monit. Scient.*, 1900, p. 563, Benker has for a number of years built chambers (in France) on the following plan:—Besides the Glover tower he employs a dry filtering chamber, in order to retain flue-dust and arsenic. His chambers are three in number, of a total capacity of only 2000 to 3000 cb.m. (70,000 to 105,000 cub. ft.). Into the last of these he introduces SO_2 (burner-gas); then comes a small intermediate chamber, and then two Gay-Lussac towers. The draught is produced by a fan-blast. Benker claims to produce 6 to 7 kg. acid of 52° Bé. (= 3·7 to 4·3 kg. H_2SO_4) per cb.m. (= 1 lb. sulphur burnt upon 13·2 to 11·3 cub. ft.!), with a consumption of 0·8 to 1·0 nitric acid 36° Bé. per 100 acid of 52° (= 3 to 3·7 lb. $NaNO_3$, per 100 S burned). The chambers are fed with a water-spray in lieu of steam (*vide infrà*), and he always injects some SO_2 (burner-gas) into the last chamber (Ger. Ps. 88368 and 91260; *cf.* later on).

Recently (*Z. angew. Chem.*, 1906, p. 137) Benker and Hartmann prefer employing *two* first chambers, upon which the gases from the Glover are equally distributed; this effects a much larger production, reduces the consumption of nitre and also the temperature.

Eliel (Amer. P. 860968) places the acid-chambers side by side between the Glover and Gay-Lussac towers. Induction and eduction flues communicate with the several chambers near the same end, the former being placed nearer the axial centre and in a higher plane than the latter. Steam-pipes open into the induction flues near their discharge ends. Means are provided for forcing the gases through these flues, producing reverse currents inwardly toward the rear, and outwardly toward the front of the chamber.

Marlow (Amer. P. 882330), in order to save space, places a certain number of lead chambers one above the other; their tops are provided with cooling-basins.

Size of the Chambers.—This varies very much. Apart from the "tambours" of the French system, the ordinary chambers are made with as little as 10,000 and as much as 140,000 cub. ft. capacity. Chambers of only 10,000 cub. ft. or little more capacity are no longer built as main chambers; the usual capacity of these may now be taken as ranging from 25,000 to 70,000 cub. ft., more frequently nearer the upper than the lower limit. Smaller chambers cost much more, comparatively, than large ones, and it is doubtful whether they afford any corresponding advantages.

The different chambers of a set are either placed on the same level, or, more suitably, each following chamber is placed 1 or 2 or, better, 3 in. higher than the preceding one, so that the acid of the back chambers can be run more easily into the working-chamber. In the first chamber the acid is both strongest and most free from nitre; and it is therefore preferable to draw off any acid from this, whether it be for sale, for use, or for concentration. The acid drawn off is replaced partly by that newly formed in the same chamber, partly by the weaker acid run over from the other chamber. If there is only one long chamber, the acid is always found strongest near the entrance of the gas.

In England, all the chambers of a set are generally of equal size, apart from local circumstances; and this plan is now more frequently used on the Continent as well than formerly, when the French system, even now the more usual, was the only one to be met with. In that system there is a "large chamber," C (Fig. 197), placed at the lowest level, combined with a few small chambers at a higher level, both before and behind the large one. Thus the first small chamber or *tambour*, A, serves for denitrating the nitrous vitriol by hot water; the second one, B, for introducing fresh nitric acid; the third and fourth tambours, E and F, for finishing the reaction.

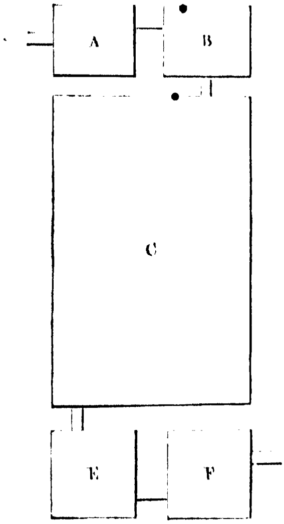


FIG. 197.

In the south of France (Favre, *Monit. Scient.*, 1876, p. 272) there was then mostly a large chamber of 135 x 26 x 20 ft., or of 100 x 16 x 22 ft., combined with two small chambers, together about 140,000 cub. ft. At Aussig each large chamber is 200 ft. long and 24 ft. wide, and is combined with a small tambour for catching the fine dust, and two small end chambers, not receiving any steam, but only serving for cooling the gas previously to its entering the Gay-Lussac tower.

Some manufacturers reject all preliminary chambers (tambours), because the chamber-process is carried on best, if a large space is afforded at once for the mutual reaction of the gases. Thus in a large French works two-thirds of the whole chamber-space are occupied by the first chamber, two-ninths by the second, and one-ninth by the third; this system is also adopted at Uetikon.

At the Government works at Oker (official communication, 1902), there are five sets of chambers, the best working of which have the following dimensions:—

Chamber I.	35 m. long,	8·00 m. wide,	6·50 m. high	=	2860 cb.m.
„ II.	30 m. „	8·00 m. „	6·50 m. „	=	1560 „
„ III.	30·15 m. „	5·49 m. „	5·25 m. „	=	869 „
					5289

The chambers communicate by pipes 1 m. wide, entering at about two-thirds of the height and going out 1·20 m. above the bottom. Small front and back chambers have been designedly left out in this system, but small back chambers exist by chance at the older sets.

Small chambers, of course, require more lead and space than large ones of equal capacity. A preliminary chamber, however, is serviceable, where no Glover tower is present, for catching the dust and cooling the gas, so as to save the large chamber. For the same reason the nitric acid was once usually introduced into a special tambour; but it is best, as we shall see, to run it down the Glover tower.

A small chamber at the exit end is certainly serviceable for drying the gases previously to their entering the Gay-Lussac towers in cases where there is no long tube or tunnel for the same purpose.

The waste of lead in small chambers is more easily understood by a definite example:—A chamber of 100 × 20 × 20 ft. has a cubical capacity of 40,000 cub. ft. and a surface of 8800 sq. ft. A tambour of 16 × 10 × 10 ft. has a capacity of 1600 cub. ft and a surface of 840 sq. ft. Its contents are therefore $\frac{1}{25}$, but its surface almost $\frac{1}{10}$ of that of the large chamber; and consequently its surface is nearly 2½ times as large, in comparison with its capacity, as that of the large chamber.

Whilst, of course, there is no doubt that a given cubic space of chamber-room is more cheaply obtained with a few large than with a greater number of small chambers, it is, on the other hand, very easy to overstep the mark in this direction. We have seen above that, in the case of chambers of an excessive section, the gases do not get properly mixed; but the same principle applies even to the division of the chamber-space in the direction of its length, since every time the gas has to be compressed into a comparatively narrow connection-tube in order to pass from one chamber to another, this must bring about a good mixture, superior to that produced in the same length of undivided chamber-space. For this reason, to begin with, it seems expedient to subdivide the chamber-space by multiplying the number of chambers; and we shall further on meet with another strong reason for the same purpose, namely, that the cooling down of the contents of the chamber, essential for the reaction among them, is promoted by their contact with the comparatively cool end-walls of the chambers.

In England it is taken as a practical rule that for every cubic foot of chamber-space there should be about 0·2 foot of total surface (top, bottom, sides, and ends). A chamber 20 x 25 x 100 feet would contain 50,000 cubic feet and have a total surface of 10,000 square feet, which is exactly the above-stated proportion. Sets of chambers in England are rarely made larger than 200,000 cubic feet; if more is required, the whole is broken up into two or more sets.

When speaking here, and elsewhere, of "chamber-gases," we always comprise in them not merely the *vapours* of water, nitrous anhydride, etc., but also the *misty* particles of liquid sulphuric acid, nitrosulphuric acid, etc., floating about in the atmosphere of the chambers.

Schertel, in fact, starting from the principle adduced by myself on an experimental and theoretical basis, to which he agrees, proposes to multiply the number of chambers, keeping them rather short (*Chem. Ind.*, 1889, p. 80). Bode (*Z. angew. Chem.*, 1890, p. 11), on the same principle, proposes chambers of half the usual length, but twice the ordinary width—say 40 ft. This would involve some difficulties, although not insuperable, in constructing the chamber-frames. Later on (Sächs, *Jahresber.*, 1890, p. 148) Schertel described practical experiments bearing out the theoretical considerations just mentioned; and further experiments on the manufacturing scale, entirely confirming my own results and conclusions, have been made by Retter (*Z. angew. Chem.*, 1891, p. 4).

Connecting-tubes.—In the usual case, where several chambers are combined to form the acid-making apparatus, the question arises how the single chambers of the set are to be connected. One thing about this is certain: that the *connecting-tubes* must be placed at the small ends, so that the gas shall travel right through the length of the chambers, and no dead corners are left. But the next question is, at what part of the section the connecting-tubes are to leave or enter the chambers. There is general consent as to this point, that the gas should enter the first chamber near its top. Some proceed in this way: they take the gas away at one end near the bottom and introduce it into the next chamber near its top. Others maintain just as strongly that this is wrong, and that, on the contrary, the gas-pipe ought to leave each chamber near its top and enter the next chamber near its bottom. Others, again, contend that it matters very little where the gas enters and leaves, and that it is therefore the simplest plan to make straight connecting-tubes about midway in the height of the chamber. This last view seems to be borne out by the practice of several practical men of very large experience, and it agrees very well with the investigations of Lunge and Naef (*vide infrà*), who found that the composition of the chamber-gases in any given cross-section of the chambers does not differ very materially between top and bottom, so that it must be indifferent where the connecting-tubes are placed. This is confirmed by information from the Rhenania works in 1902.

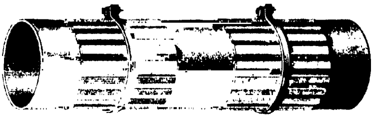


FIG. 198.

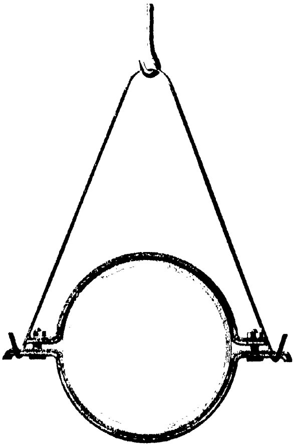


FIG. 199.

The connecting-tubes may be round pipes or angular flues (tunnels). The former are preferable, because they can be made without a frame, and because they stand better. They must, however, be made of strong lead, say 9 to 12 lb. per square foot, and bound here and there with iron hoops, between which and the lead, wooden staves are placed in order to keep the pipes in shape; but if the weight of the lead amounts to 15 lb. per square foot, no staves are needed. Figs. 198 and 199 will make this clearer.

The iron hoops serve also for suspending the pipes from beams, etc. The *width* of the pipe introducing the gas into the first chamber, whether it comes from the Glover tower or from the burners, must be adapted to the quantity of gas conveyed. For a combustion of 7 tons pyrites daily, a pipe of 2 ft. diameter; for 9 tons, one of 2½ ft.; upwards of that, one of 3 ft. diameter will do; more than 10 tons are rarely consumed for a single set in twenty-four hours. Since the volume of the gas decreases in its onward journey, the connecting-pipes between the single chambers may be successively a little smaller; but it is not well to grudge anything here, since no harm is done if the pipes are too large, but very much if they are too small.

At Griesheim several connecting-tubes are introduced between the chambers instead of one. This seems very rational, and at the same time serves for partially cooling the gases in their transit, which we shall find further on to be an important feature. "Dead corners" are most easily avoided by this plan.

According to the B. P. 20012 of 1904, of G. E. and A. R. Davis, the chambers are connected by tubes of 2 or 3 in. diameter, of which forty (more or less) are employed, so as to offer the necessary space for the gases to travel through. They are stated to have a very efficient cooling action, being exposed to the atmosphere (this is, as we see, identical with the just-mentioned Griesheim plan, described already in our edition of 1903, vol. i. p. 465).

In the 41*st Alkali Report*, pp. 91 and 92, it is stated that several firms had changed the connections of the chambers in such way that the inlet is near the bottom, and this has been found very satisfactory. The steam is introduced above the inlet and below the outlet.

Porter (*Chem. Trade J.*, 1909, xliv. p. 79) strongly recommends placing the entrance-pipe for the burner-gas at one end of the chamber near the bottom, not, as is found in most places, in the centre or near the top. His opinion is founded on experiments made with a glass model on a scale of ¼ in. to 1 ft. The exit-pipe should be about half-way up the middle at the other end.

Cellarius (Ger. Ps. 166745 and 183097) causes the gases, passing from one chamber into another, to form strong whirls by means of the centrifugal action of a steam-pipe, and to be thrown against a layer of coke, wetted with acid, or through two concentric cylinders with perforated horizontal diaphragms, for the purpose of precipitating the already formed sulphuric acid present in the state of fog.

Höfling (Ger. P. 202631) places in the entrance- and connecting-pipes of the chambers spiral-shaped plates, in order to give a rotating movement to the gases. In case of several entrance-pipes (which may be arranged in an angle to one another) the spirals are made, one turning to the right, the other to the left, so as to produce a more intimate friction and mixture of the gases.

Winsloe and Hart (B. P. 26916 of 1902) place in the pipes or trunks connecting the lead chambers or towers numerous vertical pipes, open at top and bottom. The gases circulating round these pipes are cooled and mixed, the process being assisted by baffle-plates at right angles to the air-tubes. Reference is made to B. P. 20142 of 1901.

Hegeler and Heinz (Amer. Ps. 728914, 752377; B. P. 254 of 1904) arrange the flues to enter the side of the chamber near the front end, and to pass out of the side at the rear end, at different levels, and transversely to the length of the system. The gases thus enter and pass out of the chambers in opposite directions, at different levels, and transversely to their general course. Their Amer. P. 765834 describes a main flue provided with a filled section and a free open section, with a fan in the free section, and a secondary flue communicating with the main flue before and after the filled section, and provided with a fan.

Lagache (Fr. P. 350363) withdraws part of the gases from the hottest, or from any part of the chamber, conducts them to a refrigerator, and takes the uncondensed cool gases back to the chamber.

Cubic Contents of Chambers.—The total cubical contents of a set of chambers must bear a certain proportion to the quantity of acid to be produced, several special circumstances modifying that proportion. Thus it is certain that for pyrites more chamber-space is needed than for sulphur; we have seen above (p. 559) that the relative proportion may be stated as 1 : 1·314. But now the question is, What is the absolute amount of space needed? Properly speaking, the connecting-pipes, if they are of great length, and the Glover and Gay-Lussac towers should also be included in the calculation, and that to a larger extent than corresponds to their cubical contents.

The consumption of nitre also influences the chamber-space; within certain limits a larger consumption of nitre may compensate for a smaller space.

Partly from this the widely divergent views on this point may be explained, but not entirely; for some manufacturers obtain about the same yield as their neighbours, possessing half as much more chamber-space, although both the pyrites and the general construction of the plant and their consumption of nitre are as nearly as possible the same. In the following remarks we shall reduce all measures to cubic feet of chamber-space required for burning 1 lb. of sulphur daily, taking, in the case of pyrites, the sulphur bought, not that actually burnt.

For some particulars concerning older methods, *cf.* second edition of this work, pp. 371 and 372; for recent ones, *suprà*, pp. 627 *et seq.* From sundry English alkali-works I can state the following spaces used in 1879 per pound of sulphur per diem:—

I.	II.	III.	IV.	V.
28	25	20	18	16 cub. ft.

I. and II. were considered too high by the chemists of the respective works themselves; but it should be stated that the same space was employed in 1864, when 30 per cent. Irish pyrites was used, for which it was more suitable. III. (viz. 20 lb.) is a proportion employed at many large works; but IV. and V. are found in works having as good a yield of acid (270 to 288 O.V.) and no larger consumption of nitre (3½ to 4 per cent.). In all cases rich Spanish or Norwegian ore was burnt, and both Gay-Lussac and Glover towers were used. From this it follows that under the same conditions 20 cub. ft. per lb. of sulphur charged is amply sufficient, and 18, or even 16, will do; but the latter certainly was at that time generally assumed to be the lowest allowable limit. This agrees with a statement of Wright's (*Chem. News*, xvi. p. 94), who demands 16 to 19·2 cub. ft.

From the *Inspectors' Alkali Reports* it will be seen that the amount of chamber-space actually employed at English works varies in a most extraordinary way, and not merely in consequence of the fact that very small works generally employ an excessive chamber-space. It is also seen from the same source that the usual assumption that less chamber-space is used with brimstone than with pyrites is altogether erroneous. We will here give merely a few figures obtained by taking averages of the single works enumerated, leaving out those burning both pyrites and brimstone, or coal-brasses, or "oxide."

In the *20th Report*, pp. 48 and 49, we find the average of 18 works burning pyrites to be 23·1 cub. ft. of chamber-space (minimum 15·5, maximum 38·4); the average of 10 works burning brimstone 29·7 cub. ft. (minimum 21·7, maximum 44·8). In the *21st Report*, pp. 20 and 21, 21 works burning pyrites average 26·6 cub. ft. (16 to 40); 15 works burning brimstone average 26·2 cub. ft. (21 to 48). On pp. 64 and 65, 22 works burning pyrites average 29·2 cub. ft. (17·3 to 43·2); 18 works burning brimstone average 31·4 cub. ft. (19·3 to 46·2). But as the great majority of these works are too small to afford a real guidance in this respect, we will quote in detail (from *21st Report*, p. 81) the figures of 15 medium and large-sized works in the Widnes district, comprising some other interesting information:—

Pyrites burnt per week. Tons.	Cub. ft. chamber-space per lb. of S burnt in 24 hours.	Nitrate of soda per cent. of sulphur burnt.	Capacities of Gay-Lussac towers per ton pyrites used per week. Cub. ft.	Total acidity of waste gases as grains SO_3 per cub. ft.
175	...	...	...	...
52	21·0	3·50	...	...
350	18·0	5·00	65·8	0·87
210	19·8	4·70	18·7	2·10
125	28·0	4·00	36·1	0·65
98	17·8	4·20	32·4	2·88
240	21·0	4·25	24·0	1·71
250	28·3	3·75	15·7	2·34
150	21·0	...	37·8	0·79
250	19·3	5·00	20·5	1·90
60	22·3	...	27·5	3·89
260	22·0	3·30	33·7	1·60
117	21·0	4·00	53·5	1·30
183	20·0	...	21·5	2·94
730	17·5	...	79·6	0·70
Total and averages 2590	21·0	4·17	44·4	1·82

The usual proportions in the south of France were stated by Favre (*Monit. Scient.*, 1876, p. 271) as follows:—Each square metre of grate-surface in the pyrites-burners daily receives 270 kg. of 40-per-cent. pyrites, and corresponds to 180 cb.m. of chamber-space. This means 1·66 cb.m. for each kg. of sulphur charged, or 26·5 cub. ft. per lb.

In the north of France I found, in 1878, about 8 cub. ft. per lb. of pyrites, or about 17 cub. ft. per lb. of sulphur charged, with good yields and low consumption of nitre, but only for low or medium temperatures; in summer, ¼ to ⅓ more chamber-space is required.

The preceding statements refer to ordinary pyrites, but when burning *poor ores for metallurgical purposes* much larger chamber-spaces have to be employed. This is made evident by the following statements which I have received respecting the production at the Oker works in 1901; the class of ores burnt there has been already described (p. 115).

No. of chamber-set.	Description of ore burnt.	Production of acid 50° Bé. per cb.m. chamber-space.	The same reduced to H_2SO_4
		Kg.	Kg.
I.	Mixed ore.	2·88	1·80
II.	Copper-ore, mixed ore, and regulus.	3·19	1·99
III.	Copper-ore and mixed ore.	3·30	2·06
IV.	Ditto.	3·33	2·08
V.	Principally copper- and lead-matte, with a little copper- and lead-ore.	2·84	1·77

The average consumption of nitrate of soda is 10 kg. per ton of acid 50° Bé. = 1·6 per cent. on H_2SO_4, or about 4·5 per cent. on the sulphur burnt, which is not too high considering the quality of the ores.

There is general agreement that diminishing the chamber-space below a certain extent leads to *increased consumption of nitre*, of which we have had instances before. Clement (*Fischer's Jahresber.*, 1899, p. 370), reasoning from the results obtained with two (small) sets of chambers at a Danish works, asserts that the consumption of nitre increases in proportion to the square of the utilisation of chamber-space, but his data are certainly insufficient to prove such a general proposition.

Furthermore, it is very important with what *temperature* the gas enters the chambers. The better it is cooled, the less volume it occupies for equal weight and the less chamber-space is required. For this reason a Glover tower, which cools the gas very completely, causes, even from this reason alone, apart from others, a saving in chamber-space. It is also well known that in winter for the same chamber-space either a good deal more pyrites can be burnt or less nitre is consumed than in summer; but there are also other reasons for this.

Sometimes the chamber-space is stated in so many cub. ft. per ton of salt-cake made per week. Hurter gives the following useful rules for converting one kind of expression into another: —Supposing the chamber-space is given in cub. ft. per lb. of sulphur burnt in twenty-four hours, you will obtain the number of cub. ft. per ton of salt-cake made in a week by multiplying by 75. Given, on the other hand, cb.m. per kg.: by multiplying by 16 you express the result in cub. ft. per lb. of sulphur, and by multiplying by 1200 you obtain the number of cub. ft. per ton of salt-cake made per week.

Intensive or High-pressure Style of working Vitriol-Chambers.

In recent times a new style of working has been introduced, first in several French works, called "*production intense*," say "forced" or "high-pressure" or "intensive" work. It consists in supplying the chambers with a greatly increased stock of nitre, without losing any of it, as all the nitre is recovered by means of largely increased Gay-Lussac and Glover towers; in this way the production may be increased to almost twice the usual amount, so that, in winter at least, a maximum of yield and a minimum consumption of nitre are attained with the extremely small chamber-space of 0·7 cb.m. per kg., or 11·2 cub. ft. per lb. of sulphur burnt. We have alluded to this style *suprà* in several places, and we shall have frequent occasion in later parts of this book to speak of this "intensive" style, which was formerly confined to French factories, but is now practised elsewhere as well.

In 1900, Pierron (*Monit. Scient.*, 1900, p. 367), stated as a *minimum* production in twenty-four hours, 2·34 kg. H_2SO_4 =

0·78 kg. sulphur burned per cb.m. = 1 lb. S per 19 cub. ft.; but at Kuhlmann's works the normal production is 2·9 kg. H_2SO_4 and Benker (p. 628) claims obtaining 3·6 to 4·2 kg. H_2SO_4 with ordinary chambers. The ordinary production can be increased by the use of artificial draught (fan-blasts), by "tangential chambers" (*cf.* p. 622), by "plate columns," and by other means described in their places.

For Germany, Niedenführ (1902) states the usual cubic space = 1·2 cb.m. per kg. of sulphur = 19 cub. ft. per lb., which is just the same as the *maximum* space allowed in France, but decidedly more than the average employed in that country, even where no "intensive production" is aimed at. But Niedenführ's statement is decidedly not valid for the most carefully managed German works, which, according to direct information, manufacture 3·5 H_2SO_4 per cb.m. of chamber-space, which is about 0·85 cb.m. per kg. of sulphur burnt, or about 14 cub. ft. per lb.

For the Rhenania works, producing their SO_2 from zinc-blende, Dr Hasenclever states as the normal production 2·5 kg. of 68° Bé. per cb.m. in twenty-four hours, with a consumption of 0·5 to 1·0 per cent. nitre per 100 acid of 60° Bé.

The following (hitherto unpublished) data have been kindly supplied to me by Mr G. E. Davis respecting the results obtained in a set of three chambers, each 120 × 20 × 18 ft., with a Glover 8½ × 22 ft. and Gay-Lussac 12 × 12 × 60 ft. This set was worked:—A. One month without the towers: pyrites burned 135 tons, potted 96 cwt., 25 cub. ft. chamber-space per lb. of sulphur in twenty-four hours; 79 lb. nitrate of soda sent into the chambers per ton of pyrites. B. One month with the towers in full operation: pyrites burned 180 tons (19 cub. ft. chamber-space per lb. sulphur), 101 cwt. $NaNO_3$ introduced by Gay-Lussac acid, 56·2 cwt. nitrate potted, 98 lb. nitrate introduced into chambers per ton of pyrites. C. One month with towers: 240 tons pyrites (= 14·4 cub. ft. per lb. sulphur), 205·6 cwt. $NaNO_3$ in Gay-Lussac acid, 86 cwt. nitrate potted, 135 lb. nitrate in gases per ton of pyrites. D. One month with towers: 302 tons pyrites (= 11·5 cub. ft. chamber-space per lb. S), 277·3 cwt. $NaNO_3$ in Gay-Lussac acid, 135·1 cwt. potted, 152 lb. total nitrate per ton of pyrites. Lastly, E. One month with towers: 380 tons pyrites (= 8·1 cub. ft. chamber-space per lb. S), 394 cwt. $NaNO_3$ in Gay-Lussac acid, 203 cwt. nitrate potted, total nitrate 176 lb. per ton of pyrites. Under the last conditions the chambers were worked for nearly a year; oxygen at burners 10 per cent., at dust-burner 12 per cent. Average acidity of gases going into Gay-Lussac 5·5 gr. H_2SO_4 per cubic foot, and gases leaving the tower 1·4 gr. H_2SO_4.

The *yield* varied very little in all these cases, viz., from 40·2 cwt. acid of 123° Tw. per ton of pyrites in A to 39·8 cwt. in E. (The above-quoted consumption of nitre is very high, even for easy work, let alone for high-pressure work.)

Mr Davis states the general opinion of English acid-makers as follows:—"If you go on in the old way, working with 25 cub. ft. of space per lb. of sulphur per twenty-four hours, the process goes on absolutely by itself. Decrease your chamber-space to 15 cub. ft., and you want a chemist and clever foreman, while with 8 cub. ft. neither foreman nor chemist knows what peace is either by night or day."

Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1334) gives the following data. With ordinary chambers frequently 3 kg. H_2SO_4 per cubic metre is made, with "intense" working up to 4 kg. With atomised water and fans (cf. *infrà*) in ordinary chambers 5·84 kg. have been obtained. A set of Meyer's chambers (p. 622) without other improvements produces 4 kg., according to Meyer's own publications up to 6·3 kg.; combined with fans and atomised water, probably up to 8 kg.

Petersen (*Z. angew. Chem.*, 1907, pp. 1101-1105) greatly recommends this high-pressure style He does not, from his experience, believe that the chambers suffer under it more than in the ordinary way, but much more nitre must be introduced.

An important paper on the "intensive" or "high-pressure" working of the acid-chambers has been published by Nemes (*Z. angew. Chem.*, 1911, pp. 387-392). He justly points out that very naturally every acid-maker wishes to make the fullest possible use of his plant; but whether it is really more economical to make from 4 to 8, or else 12 kg. chamber-acid per cubic metre of chamber-space, is a question not yet finally decided. Concerning the history of the "intensive" chamber working, the author quotes from the German edition of my *Sulphuric Acid and Alkali* (third English edition of 1903, vol. i. pp. 453 and 468) statements on the high-pressure style in England and France which I had received from private sources, and he himself quotes experiments made in that direction by the St Gobain factory on a large scale. According to him, the stimulus for a further progress in that direction came, in 1900, from the facts then becoming known on the contact process of the Badische Anilin- und Sodafabrik, which was soon followed by others. In that year the minimum production of ordinary chambers in France is stated by Pierron at 2·34 kg. H_2SO_4 per cb.m.; the Benker chambers (p. 628) producing 3·6 to 4·0, and Meyer's tangential chambers 3·2 to 3·4, Falding's chambers (*vide infrà*) even 6·2 kg. H_2SO_4. In 1902 Lüty and Niedenführ report on their results, and the former speaks of 12 kg. chamber-acid (=7·4 kg. H_2SO_4), but without saying anything on the consumption of nitre and on the life of the chambers. Hartmann and Benker, in 1903 and 1904, speak of 3·98 to 4·58 kg. H_2SO_4 with an expenditure of 1 per cent. nitrate, and later on of 8·5 to 8·75 kg. H_2SO_4 with a use of 0·7 to 1·1 per cent. nitre, but say nothing on the life and the repairs of the chambers. On Meyer's tangential chambers, Hess reports in 1905 (*Z. angew. Chem.*, xviii. p. 376), after five years' experience, a production of 3·75 kg. H_2SO_4 per cubic metre, with an expenditure of 0·54 parts nitre on 100 parts chamber-acid, or nearly 1 per cent. on the real H_2SO_4 produced. Nemes then refers to the controversy between Lüty, Niedenführ, Neumann, and Petersen, on which we shall report later on in connection with the new style of working the Gay-Lussac and Glover towers, and he justly remarks that chambers working-up poor and irregular gases from metal-smelting works, with an expenditure of 2·7 per cent. nitre, must necessarily waste the chamber-lead more than the "intensive" style with ordinary gases and with 1·1 per cent. nitre. He further quotes the statements of Schmiedel (*Z. angew. Chem.*, 1908, p. 249), of Proelss (*Chem. Zeit.*, 1910, p. 322), who required 2·2 per cent. nitre for 4·35 kg. H_2SO_4 and 3·51 per cent. nitre for 7·24 kg. H_2SO_4 per cubic metre, and of Opl (*Z. angew. Chem.*, 1909, p. 1961) on the Hruschau process, where 31·2 kg. H_2SO_4 per cubic metre were produced in towers, with an expenditure of 0·72 per cent. nitre.

Nemes further reports on the work carried on in a number of cases known to him personally. The following table represents the results obtained:—

Factory.	Kg. H_2SO_4 made per cb.m.	Kg. nitric acid 36° Bé. consumed per 100 kg. H_2SO_4	Life of the chambers. Years.	Country.
A	2·20—2·40	0·58—0·64	18—20	Belgium.
B	2·34	0·51	20	Rhineland.
C	3·74	1·01	15—17	France.
D	3·75	1·76	...	Rhineland.
E	5·00	1·28	...	?
F	5·94	2·88	8—10	Eastern Germany.
G	6·25	2·64	...	Austria.

These works represent various types, and evidently the results depend very much on the style of work, the raw materials, the plant, etc. But it is a rule without exception that the consumption of nitric acid increases with the increase of production per cubic metre, and that in much higher proportion when the production is strongly forced up. Nemes says that the consumption of nitric acid in systems of entirely different construction may be represented by the following oscillations:—

Kg. H_2SO_4 made per cb.m.	Kg. nitric acid used per 100 H_2SO_4.
3	0·35—0·55
4	0·50—0·70
5	0·60—0·90
6	0·70—1·10
7—8	0·80—1·30
8—9	1·00—1·60
9—10	1·20—1·80
10—12	1·50—2·00

The oscillations of the consumption of nitric acid in the intensive style are greater than with small production.

The *cost of repairs* naturally varies very much, but undoubtedly is much higher when making 10 to 12 than when normally making 5 kg. acid per cubic metre. Lüty and Niedenführ's figure (*Z. angew. Chem.*, 1902, p. 272), say £600, appears rather too low than too high, and will certainly not suffice for a high-pressure set producing 50 tons H_2SO_4 per day, as assumed by Lüty (*ibid.*, 1905, p. 1257).

Nemes further states the *cost of plant* for a daily make of 30 tons chamber-acid for four cases known to him by experience; all of them provided with Glover and two Gay-Lussac's fan, water-spray, etc., but with considerable differences of production. The cost of machinery, buildings, and furnaces is about the same for the same production, but the cost of the chamber-frames and that of the lead differs considerably. The cost is stated in marks (1·02 = 1s.):—

		No. 1.	No. 2.	No. 3.	No. 4
Reduction of chamber-acid per cb.m., kg.		3	5	8	10
Cubic contents of chambers, in cb.m.		10,000	6,000	3,750	3,000
Ground space required for chambers, superf. m.*		1,100	720	480	400
Value of ground space	marks	52,000	44,000	39,000	38,000
Buildings	,,	50,000	50,000	50,000	50,000
Machinery	,,	18,000	18,000	18,000	18,000
Pyrites kilns	,,	50,000	50,000	50,000	50,000
Value of lead	,,	120,000	84,000	50,000	40,000
Towers and chamber-frames	,,	180,000	100,000	75,000	60,000
Altogether		470,000	346,000	282,000	256,000

* The total ground of the factory may be put ·5 times the above figure.

Nemes now calculates, starting from these assumed costs of plant, the *cost of producing the acid.* He assumes the consumption of nitric acid,

	For No. 1.	For No. 2.	For No. 3.	For No. 4.
per 100 kg. H_2SO_4	0·60	0·88	1·76	2·40 kg.

which, as he considers, is rather too favourable for the intensive style (Nos. 3 and 4); coals = 14 per cent. to 200 H_2SO_4; labour, ten men at 4 marks; repairs, according to practical experience, inclusive of repacking towers, fans, etc. Capital interest, 5 per cent.:—

	4000	5000	9000	12,000 marks.
The life of the chambers he puts at	20	16	12½	10 years.
Hence, the percentage of capital amortisation	5	7·6	8	10 per cent.

In the amounts for amortisation no account is taken of the ground-space and 70 per cent. of the lead, leaving 15 per cent.

for loss in remelting and 15 per cent. for the cost of that process. This leads to the following figures for the cost of making sulphuric acid in those four plants, in the shape of chamber-acid, but calculated upon real H_2SO_4 :—

H_2SO_4 produced per ch.m.—kg.	1·87	3·28	5·00	6·26
	Marks.			
Sulphur (as pyrites)	1·280	1·280	1·280	1·280
Nitric acid	0·120	0·176	0·352	0·480
Power and light	0·200	0·200	0·220	0·220
Wages	0·210	0·210	0·210	0·210
Repairs	0·060	0·073	0·131	0·189
Amortisation	0·245	0·225	0·193	0·193
Interest	0·345	0·252	0·206	0·187
Total	2·460	2·416	2·592	2·749
Cost price of H_2SO_4 in the form of chamber-acid	1·538	1·510	1·620	1·720

This does not include general expenses (for management, etc.), which may be taken to be the same in all cases. The total capital required may be put = 600,000 marks for the high-pressure system, against 700,000 marks for the ordinary system.

The final result of these calculations, which Nemes declares to be founded on practically obtained results, is this: that, contrary to the general assumption, *the intensive or high-pressure style of working the chambers leads to higher costs of producing the acid than a normal production* of about 6 kg. chamber-acid per cubic metre, owing partly to the comparatively great wear and tear and the consequent higher cost of amortisation and repairs, partly to the increased consumption of nitric acid. It is now a proven fact that in the high-pressure style there is greater wear and tear of the lead, for the temperature is higher and the amount of nitric acid in circulation is greater; there is also a greater quantity of sulphuric acid condensed on the lead, which washes off the protecting coat of lead-mud. The conclusion is: that for new erections the intensive style should not be chosen, and the adoption of this style can be advised only for special cases, such as the impossibility of enlarging a factory, or special conditions of trade, or the stoppage of another set of chambers for repairs, and so forth.

Finally, Nemes briefly discusses the question how matters stand when comparing the manufacture of sulphuric acid in chambers with the production of sulphuric acid without chambers, in towers, etc., as described in a following chapter. He considers that it is as yet too early to come to a definite conclusion on this point, and several years' further experience is required before the cost of acid by these systems can be definitely calculated.

Petersen (*Z. angew. Chem.*, 1911, pp. 877-881) very strongly opposes the statements and views of Nemes, and his comparative tables on the expenses of erecting and working chambers by different systems, which are calculated on quite arbitrary assumptions as to the costs of repairs and the life of the chambers. He also objects to his basing his comparison of the consumption of nitric acid in the various systems on antiquated data. Nowadays factories producing 8 to 10 kg. acid 50° Bé. per cubic metre of chamber-space should in no case use more than 1 per cent. nitric acid 36 Bé., and he quotes a case where only 0·6 per cent. was used by the Falding system (*vide infra*); only 0·8 per cent. nitric acid 36° Bé. is required for producing up to 11 kg. sulphuric acid 50° Bé. per cubic metre. Petersen considers the principal advantage of the high-pressure system to be the saving of 30 to 50 per cent. capital, which allows quicker amortisation. He concludes with a comparison of Meyer's and Falding's chambers, which we quote when treating of the latter.

Th. Meyer (*Z. angew. Chem.*, 1911, p. 1520) points out that "intensive work" can be produced by various styles of apparatus, but will be always connected with a greater expenditure for nitre and repairs, and that the optimum of work will lie between the extremes.

Nemes (*ibid.*, p. 1564) replies to various criticisms of his paper, and insists that the producing-cost in the system advocated by him is no higher than in the ordinary style of work.

Hartmann (*ibid.*, p. 2302) states that it is possible to keep up good working of the chambers even when going up to a production of 12 kg. acid of 53° Bé. per cubic metre, as far as the consumption of nitric acid, high-pressure air, cooling-water and wages is concerned, but that the advantage is partly, sometimes even more than completely counterbalanced by a considerably quicker and higher wear and tear of the chambers. Hence such intense working of the chambers has now been given up again, and a production of 7 kg. acid of 53° Bé. per cubic metre may be taken as normal now. The Glover towers have not been worn out more quickly than otherwise, even by the intense work.

Hasenclever in 1911 (*J. Soc. Chem. Ind.*, 1911, p. 1292) considers it advisable to be satisfied with a production of 5 to 6 kg. acid of 60° Bé. per cubic metre of chamber-space, or, expressed in British units, about 11 cub. ft. of chamber-space per lb. of sulphur burnt in twenty-four hours; when increasing the production above this, the cost of chamber repairs rises immensely.

In the brief summary of the, partly very vehement, discussion on the advantages and drawbacks of the "intensive" style of working the chambers we have tried to preserve entire impartiality, but in conclusion we must state our impression that that style is more and more extending, and just the most advanced manufacturers of sulphuric acid seem decidedly on the side of the "intensive" work. According to the *47th Official Report on Alkali Works*, 1911, p. 15, that system is working without any undue escape, the acidity of the gases, with efficient supervision, being well within the limits prescribed and varying but little from the ordinary practice.

Other Proposals for Diminishing the Chamber-space.

The considerable ground-space taken up by the ordinary vitriol-chambers, and the very large capital required for these immense leaden structures on the Continent, also the expense of the correspondingly vast buildings containing them, has led to a great many proposals for restricting the chamber-space, or for doing away with lead chambers entirely and substituting cheaper apparatus for them.

One way of greatly diminishing the space required for the reactions of the vitriol-making process would be to use *pure oxygen* instead of air for oxidising the sulphur. This, indeed, forms the subject of patents by Terrell, Hogg, and Tomlinson (1871), and of A. & L. Q. Brin (B. P. 12070 of 1886); also by Ellice Clark, as communication from G. Lunge (B. P. 3177. 1888; *cf.* also Bode, in *Dingl. polyt. J.*, ccxvi., p. 453); but it is unlikely that by any mode of manufacture whatever will oxygen become cheap enough to serve for making ordinary sulphuric acid.

Scheurer-Kestner (*Bull. Soc. Ind. Mulhouse*, 1890, p. 276) calculates the cost of 490 kg. oxygen, corresponding to a metrical ton of sulphuric acid, at 176 frs. = £7, which of course renders the employment of such oxygen entirely out of the question. Oxygen is now cheaper than at that time, but even in the shape of "Linde's air," or of the cheapest electrolytic oxygen, its price is prohibitive.

Another way of increasing the production of acid for a given chamber-space is by producing *a better mixture of the gases within the chambers*. Some of the proposals in this direction are combined with the *cooling action* demanded by the theories to be explained in Chapter VII.

Most proposals for manufacturing sulphuric acid in a diminished space start upon the assumption that in the ordinary vast chambers the gases are not sufficiently well mixed; some of them also on the supposition that there is not enough "condensing" surface for the sulphuric acid, and that this should be artificially increased. So far as it was assumed that the sulphuric acid required to be condensed from a vapour into a liquid, similar to the condensation in distilling alcohol, etc., this theory is, of course, wrong, inasmuch as the sulphuric acid is liquid as soon as formed, and does not exist at all in the chambers in the state of vapour. But we shall see further on that for other reasons it is certainly true that a large amount of *surface* for the chamber-gases to impinge on is indeed a most important factor in the chamber-process, and that, moreover, a certain amount of *cooling* is also of great importance in this respect. We shall see that this proceeds from the necessity of bringing about the reaction between the nitrososulphuric acid and the liquid water or dilute sulphuric acid floating about in the chamber. Whilst, therefore, we must acknowledge that former inventors were on the right track when increasing the surfaces of contact, it is a fact that their efforts were unsuccessful; but this was caused by the circumstance that they did not (and could not in the then state of the subject) properly understand the essence of the process, and that they consequently chose the wrong means for their ends. Partitions within the chambers, if made of lead, are most quickly corroded; if made of glass, they soon collapse (*vide* p. 650).

Ward (B. P. 1006 of 1861) proposes a special mixing-chamber for the combustion of 7 tons pyrites in twenty-four hours, 64 ft. long, 16 ft. high, and 20 ft. wide, followed by a second lead chamber, or flue, 200 ft. long by 3 ft. high and 3 ft. wide, almost filled up with sheets of glass to a length of 25 ft. The sheets lie in a horizontal position, and are kept a little apart by strips of glass, to permit the passage of the gases. Ward believed that upon these sheets (in lieu of which tubes might be used) nitrous vitriol would condense and afford a large surface to the sulphurous acid. His plan does not appear to have been carried out in practice, or if it was it must have been abandoned again, probably because his erection possessed too little stability or was too easily stopped up. The horizontal arrangement is also unfavourable to a systematic action of the gaseous and liquid agents, for which streams in opposite directions (up and down) are preferable, as we shall see below; and the total lack of a cooling arrangement would make the whole principle of reaction on the solid surfaces incomplete, as will be shown later on.

Mactear (*J. Soc. Chem. Ind.*, 1884, p. 228) carried out some experiments showing the importance of surface condensation. A tray, placed in a vitriol-chamber, 1 sq. ft. area, was found to give 708 g. H_2SO_4 in twenty-four hours. By placing in the tray twelve pieces of glass, 12 in. by 6 in. each, in a vertical position, the amount of acid obtained in twenty-four hours rose to 1644 g., or 2·3 times as much, and by placing the glass slips horizontally, the same distance apart as before, the make of acid rose to 3226 g., or 4·5 times more than without the glass. Other experiments made with "surface condensers" within the chambers showed that in the case of flat vertically placed sheets the side facing the gaseous current condensed more acid than the opposite side, in the proportion of 100 : 78. When the same plates were placed horizontally, with their edges facing the current of the gases, the amount obtained from the double surface was 172, against 178 in the former case.

The principle of surface condensation is also employed in de Hemptinne's chamber-system, which will be mentioned in Chapter IX., in connection with his system of concentration.

At some places, *e.g.* at Uetikon near Zurich, there existed for a time a peculiar kind of chambers. Each set consisted of only one large chamber, 330 ft. long; within this, however, there were two partitions, dividing it really into three chambers. The partitions are made as shown in Fig. 200. A row of perpendicular iron gas-tubes of 1-in. bore, covered with lead, *a*, is placed across the chamber, carried through its top, *b*, and hung from one of the joists, *c*. At vertical distances of 2 ft. there are lead hooks, *d d*, attached to the tubes, on the opposite side other hooks, *d' d'*, a little lower. These hooks must not be made of sheet-lead, because they bend too easily, but they must be cast. On these hooks sheets of glass 2 ft. + 2 ft. 6 in. are placed loosely, leaving chinks of about 1 in. width for the passage of the gases, in order to mix them better. These partitions do not seem to offer any guarantee of durability; and in fact, both at Uetikon and at other works, formerly possessing similar glass partitions, they have been removed again; they are said to have sometimes suddenly collapsed and cut through the chamber bottom.

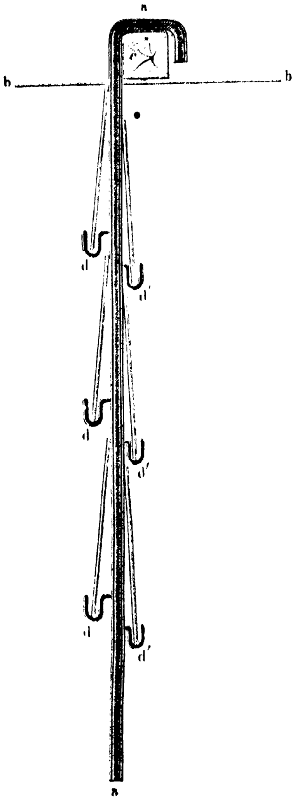


FIG. 200.

The simplest kind of internal partition—viz. sheets of lead—is not practicable, because the lead, exposed to the heat and the gas on both sides, is very quickly worn away. This entirely disposes of the suggestion of Bornträger (*Chem. Ind.*, 1885, p. 386) to make nearly horizontal (rather slanting) partitions in the chambers, in order to multiply contact-surfaces. Both in this case and in the Uetikon plan the internal contact-surfaces, not being cooled, do very little service (*cf.* later on).

Walter and Boeing (Ger. P. 71908) employ hollow partitions, made of acid-proof material, arranged across the whole width of the chambers. Double walls are constructed of such a form that the principal gaseous current enters through large holes near the bottom, rises upwards in the space between the walls, and issues at the top; at the same time the gases are allowed to penetrate into the inner space by numerous small openings, and to issue in the same way on the other side, so as to produce a good mixture. Buttresses and binders produce sufficient stability without interfering with the draught, which is also procured by making the sectional area of the openings and joints much larger than that of ordinary connecting-pipes. [This system aims at attaining the same object as the previously introduced plate-columns in a simpler way. But, in consequence of the many outlets offered to the gases, it is doubtful whether they will travel exactly in the desired path. The stability of such inner walls, even when made of the best material, is very doubtful indeed, and a collapse must produce most disastrous results, as has been found in practice, wherefore the use of these partitions has been abandoned.]

Brulfer (Fr. P. 220402) also employs hollow brick partitions within the chambers; he adds dividing apparatus, made of air-cooled lead tubes, fixed behind each partition. When the gases have passed through a cooled divider, they again pass through a hollow brick divider.

Olga Niedenführ (Ger. P. 241894) employs partitions of lead-covered iron which are placed in the chambers and divides these into single elements which can be combined or separated at will.

A similar principle, in which, however, the idea of mixing the gases was the chief aim of the inventors, is involved in the proposal made by Gossage and many others, and frequently carried out in practice, of *filling the chambers partially or entirely with coke*, or of erecting special coke-towers at the end of the set, not as Gay-Lussac towers, but to be merely moistened by water or steam. In practice it has been found that even as a matter of construction this plan gave much trouble, because the great weight pressing upon the outside layers of the coke makes it bulge out or even cut through the chamber sides. But apart from this it was found that the yield of acid for a given chamber-space was *not* increased, that more nitre was consumed, and that the acid was rendered impure by the coke. Everywhere, therefore, the coke has been removed again from the chambers themselves, and has been relegated to its legitimate place in the Gay-Lussac tower. The cause of this failure is probably twofold: firstly, the injurious action of the coke on the nitrous gases, which would thereby be reduced with formation of carbonic acid (*cf.* Chapter VI.); secondly, the lack of any cooling, just as in Ward's case (p. 649).

The same objections hold good for the apparatus of Verstraet (*Bull. Soc. d'encourag.* 1865, p. 531), which was worked in Paris for some time, but had to be abandoned as impracticable. It consisted of a number of stoneware jars without a bottom, covered 430 sq. ft of ground, cost only £280, and was to supply daily a ton of sulphuric acid of 106° Tw. There were twelve perpendicular stacks of five jars each, filled with coke and traversed by the burner-gas; nitric acid ran down over one of them, meeting the sulphur dioxide; and the resulting acid was run over the other stacks in regular rotation.

The apparatus of Lardani and Susini (*Bull. Soc. Chim.*, viii. p. 295) was founded on the same principle. Its peculiarity is a "reaction-apparatus," whose lower part is filled with sulphuric acid, on the top of which a thick layer of nitric acid is floating; the upper part, divided from the lower by a perforated partition, is filled with pumice; the nitre-gas is regenerated to nitric acid by an excess of air and water in a system of pipes filled with pumice or coke.

Mechanical Gas-mixers.—That mixing the gases alone is not sufficient is proved by the small success of Richter's apparatus (Ger. P. 15252), consisting of a steam-injector on the top of the chamber, which aspirates the gases from the lower part of the chamber and reintroduces them at the top. It is true that by this apparatus probably only a small portion of the gases would be set into circulation; otherwise the draught would have been interfered with in an intolerable way. At all events no great advantage has been obtained by using it in all the factories visited by me; but at some places a certain improvement is said to have been produced by this means.

The same proposal has been made in a somewhat modified shape by N. P. Pratt (B. P. 4856 of 1895). He places a fan or steam-injector in front of the chamber, and a tower, fed with weak sulphuric acid, at the end of the chamber, the gases issuing from the top of this tower being re-injected into the chamber by means of the fan. Baffling-columns may also be placed within the chamber. Modifications of this system by the same inventor are described in the Amer. Ps. 652687 to 652690, and B. P. 10757 of 1899.

Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1332) recommends also placing the mixing-fans in front of the chambers, not, as some have done, at the end of it.

Rabe (Ger. P. 237561) produces in vitriol-chambers a movement of the gases according to the theory of Abraham, to be explained in Chapter VII., viz., in a spiral way, by mechanical means, or by means of sprays of cooled sulphuric acid of lower strength than chamber-acid, the spray being produced by chamber-gases. A further patent of his (Ger. P. 240474) tries to produce the mixing of the gases in another way. In order to prevent the hot gases, coming from the Glover tower, to flow along the top of the chamber, partitions are provided at right angles to the direction of the gaseous current, reaching some distance downwards from the chamber top (from which they are suspended), and, if necessary, cooled by water. Or else a similar effect is produced by making the chamber ceiling inclined from the entrance to the outlet end.

Th. Meyer's "tangential chambers" also belong to this class of apparatus (*cf.* p. 622).

Dr Burgemeister (private communication) proposed both to *mix and to cool* the gases by arranging a number of lead pipes, 15 to 18 in. wide, vertically between top and bottom of the first chamber, and cooling these by air passed through. This plan is hardly practicable, as the immense extension of joints, especially at the bottom, will cause too many interruptions for repairs; but it can be more easily carried out, according to Hartmann (*Chem. Zeit.*, 1897, p. 877), by constructing these inner pipes or shafts in the same manner as an ordinary chamber bottom, that is with a hydraulic lute, formed by turning up the chamber bottom round the bottom of the pipes. Hartmann employed a number of such shafts, 5 × 6 ft. wide, and thereby obtained an increase in the production amounting to 20 per cent., viz. 0·9 to 1·0 cb.m. chamber-space per 1·0 kg. sulphur burned. [This is not particularly high.]

Evers (Ger. P. 151723) describes an apparatus for mixing the gases, consisting of specially constructed tubes within the chambers.

F. Blau (Ger. P. 95083) injects a spray of cooled sulphuric acid into the first hot part of the lead chambers, in order to keep down the temperature, and a spray of hot acid into the last part of the chambers where the reaction is sluggish and is to be revived in this manner. If the exit-gases thereby become too hot, they are cooled by a spray of cold acid before entering the Gay-Lussac tower.

Fromont (B. P. 4861 of 1907; Ger. P. 191723), for the purpose of promoting the removal of the heat and thus condensing water or dilute acid, makes the walls of the chambers of corrugated sheets of lead, the metallic shine of which has been removed by producing a rough surface; the chambers are moreover fitted with inward lead baffles, soldered on perpendicularly to the face of the side. The roof of the chamber is for the same purpose shaped in an elliptical form, and inside the chambers diaphragms are arranged for increasing the surface.

O. H. Eliel (Amer. P. 860968) describes lead chambers about three times as long as wide. The pipe coming from the Glover tower enters the end-wall of the first chamber in the centre of the width, about one-third of the height from the bottom, and inside the chamber it is conically contracted. At a lower level of the chamber end two pipes take the gases out and carry them into the next chamber, after having joined in a common pipe which ends conically within the second chamber, like the gas-pipe from the Glover tower. Precisely in the same way the gases are taken out of the second into the third chamber, and from this into the Gay-Lussac tower, so that all this piping is located at one end of the chambers, only at different levels. Steam-pipes are arranged in the centre of all the entrance pipes.

A new style of chambers has been introduced by Fred J. Falding, 55 Broadway, New York (Amer. P. 932771 of 1909; B. P. 26452 of 1909; Fr. P. 410556; Ger. P. 241509), about which he reports in *Eng. and Min. J.*, 1909, pp. 441 *et seq.*; and *J. Soc. Chem. Ind.*, 1909, p. 1032. Starting from considerations as to the production of heat in the process and to the convection currents set up thereby, he employs only one chamber (together with a cooler) of much greater height than had been attempted hitherto, up to 70 ft., with a horizontal section of 50 × 50 ft., and he makes the following comparison of the surface area of lead (7 lb. per superficial foot in all cases) required for the same effect:—

(1) Chambers built by himself near Pittsburg and in Tennessee. Capacity 175,000 cub. ft. (4952·5 cb.m.), 19,000 sq. ft. 7 lb. lead = 66·5 short tons (1765 sq. met. = 60·315 met. tons).

(2) Chambers erected by Dr Theodor Meyer's tangential plan (*suprà*, p. 622). Capacity 174,480 cub. ft., 31,412 sq. ft. 7 lb. lead = 110 short tons (2918 sq. met. = 99·77 met. tons).

(3) Ordinary horizontal chambers, 174,960 cub. ft. = 32,004 sq. ft. 7 lb. lead = 112 short tons (2973 sq. met. = 101·584 met. tons).

This shows a saving of about 40 per cent. of lead in high chambers of Falding's system for the same cubic capacity and irrespective of the increased efficiency of chamber-space. It is true that in his system the gases leave the chambers too moist and too hot to permit their direct admission to the Gay-Lussac towers, and they must be dried and cooled first; but this can be done with much greater economy than by providing additional chamber-space. The results quoted from actual work are very satisfactory; there is no SO_2 left over when the gases leave the chamber, and the consumption of nitrate is reasonably low. The saving in ground-space is about 60 per cent. The chambers are erected on a slab of reinforced concrete, covered with ¾ in. asphalt, perfectly smooth, in order to receive the bottom lead of the chamber. The framework consists of steel side-trusses with Z-bar posts, bolted to anchorage in concrete piers, and connected by angle-iron horizontal bars, which are connected with the walls of the chamber by continuous horizontal lead straps, burned to the lead sides and clamped and bolted to the angle-iron girts in such manner that the angle-iron is in contact with the strap only and does not touch the lead sheets. The roof trusses are connected by angle-iron joists. The framework is rigid and strong and affords easy access for repairs and painting; it comes at no point in contact with the chamber-lead.

The chamber-system consists of a cooler and a single high, tower-like chamber, into which the reacting gases are introduced at the top, and from which they are taken away at the bottom. The proportion of height to the diameter is as 3 : 2. The gases go first through a Glover tower, then into the chamber, then into a small cooling-chamber (also entering at the top), and at last into a Gay-Lussac tower. The cooling-chamber and the Gay-Lussac are cooled by running water over them ; the large chamber is not cooled, but sprayed with nitrous vitriol.

Petersen (*Z. angew. Chem.*, 1911, p. 880) compares the systems of Falding and of Th. Meyer (*tangential chambers*, p. 622) as follows:—(1) The production in Falding's chambers, for the same consumption of nitre, is greater than in Meyer's chambers ; (2) The former require only about half as much ground-space as the latter ; (3) The action of the gases on the chamber-lead is much less in Falding's system, where the gases descend uniformly in the chamber, than in Meyer's system, where they are as much as possible brought into contact with the chamber walls; (4) Much less lead is required by Falding than by Meyer, as proved by the figures given above. Petersen repeats his commendation of Falding's chamber against the remarks of Th. Meyer in *Z. angew. Chem.*, 1911, p. 1520, *eodem loco*, p. 1811.

Intermediate ("Reaction") Towers.

A further way for increasing the production of acid is the employment of special *mixing and cooling towers and columns* between the chambers, even to the exclusion of all chambers except a first and perhaps a last small chamber. These "intermediate" or "reaction" towers have had the greatest success in diminishing the space for the production of sulphuric acid.

One of the first attempts in this direction was the plan of Thyss (Ger. P. 30211), of which I have myself given a detailed description in *Z. angew. Chem.*, 1889, p. 265, abstracted in the second edition of this treatise, pp. 378 and 379. This system having completely broken down after a short trial, it may suffice to say that Thyss employed lead towers, provided with a number of perforated lead shelves over which the gas had to take a zigzag course. These towers were not fed with any liquid, and consequently they must have become very hot and could exert no cooling action; the draught was very much impeded and the lead quickly corroded. Moreover, these towers cost twice as much as an ordinary chamber producing the same amount of acid. Still, although the Thyss columns were both an economic and a technical failure, they proved that even in that imperfect form an intimate mixture of the gases and their contact with solid surfaces considerably hasten the reaction.

Much better elaborated was the plan of Sorel (Fr. P. of 1886; *cf.* his *Fabrication d'Acide sulfurique*, p. 398, and *Z. angew. Chem.*, 1889, p. 279). He proposed to start with a small chamber; from this the gases were to pass through cooling-pipes and then through two or three towers, where steam is also injected, while acid of 142° to 150° Tw. is running down, the out-flowing acid not to fall below 130° Tw. Although he was then connected with one of the largest chemical works in the world, his proposal has never been tried on the large scale, probably owing to constructive difficulties; moreover, his idea of employing *strong* acid for feeding the towers would rob the process of most of the advantages of the principle.

Lunge's Plate-towers.—It is probably generally (most recently again by Hartmann in *Z. angew. Chem.*, 1911, p. 2303) recognised that the object in question was first fully accomplished by my *plate-towers* (*Z. angew. Chem.*, 1889, p. 385), in which I endeavoured to combine all the principles hitherto recognised as paramount in the manufacture of sulphuric acid. In Chapter VII., when treating of the theory of the chamber-process, we shall see that I formulate this theory as follows:—Nitrous acid (or anhydride), or in the first part of the chambers nitric oxide, acts as carrier of atmospheric oxygen and water upon sulphur dioxide, by which action nitrososulphuric acid is formed. This acid, which for the most part at once dissolves in the sulphuric acid already present, like this floats about in the chamber in the shape of a fine mist. When coming into contact with water, or, which is probably the usual case, with dilute sulphuric acid, a decomposition takes place by which sulphuric acid is formed, and all the nitrous acid is returned into the atmosphere of the chamber to recommence the above-described action.

It is evident that all these reactions require in the first instance a most intimate and constantly renewed *mixture* of all the gases, vapours, and misty particles. In the ordinary large chambers a long course, a vast space, and a correspondingly long time are needed till the reactions are practically complete; that is, till nearly all the SO_2 has been removed from the gases. If it were only the question of a mixture of gases and vapours, probably very much less time and space would be required; but as both the nitrososulphuric acid and the dilute sulphuric acid, which are to act upon each other, are in the state of mist, that is, of minute *liquid* drops, they may travel for some distance side by side without coming into actual contact and reacting as they are intended to do. In many similar cases it has been found that simply mixing up the atmosphere in question is nothing like so efficient as presenting large *solid* (or liquid) *surfaces* against which the gaseous current must strike in its progress. By the shock against these surfaces, and the loss of velocity thereby incurred, and undoubtedly also by surface attraction, the misty particles which would otherwise float about for hours in the same state are condensed on those surfaces in larger drops or films, and then the mutual reaction above described, leading to the splitting up of nitrososulphuric acid, will take place at once. From this we infer that we ought to arrange a number of large solid surfaces in the path of the gaseous current, in such manner that this current must continually strike against them and be constantly broken up into small parts and mixed up again. (In this respect Ward's glass sheets, p. 649, running parallel with the gaseous current, were not properly disposed.)

There is, however, another condition to be realised for a proper working of the chamber-process. As we shall see further on, it is indispensable that the *temperature* of the chamber be kept sufficiently low to condense the requisite quantity of aqueous vapour into liquid water or dilute acid, sufficient for decomposing the nitrososulphuric acid. As the reactions in progress within the chambers produce a large quantity of heat, the process cannot go on without a portion of that heat being abstracted again, which in the ordinary system is done by radiation from the chamber sides. The separation of the whole chamber-space into several smaller chambers acts favourably in this respect, as the ends of the chambers and the connecting-pipes act as cooling-surfaces; and Sorel (p. 657) actually proposed increasing this by arranging a set of cooling-pipes, which, however, would be nothing like sufficient for the purpose. My own plan is, however, different from anything proposed up to that time. I effect the necessary lowering of the temperature, not by radiation or convection to the outer air, but from within by a shower of water or very dilute sulphuric acid. Thus several objects are attained at the same time. The temperature of the chamber atmosphere is reduced to a proper level, parts of its heat being spent in heating and vaporising water; but this water is just what is required for carrying on the chamber-process itself, and thus a saving is effected in the raising of steam for the purpose of supplying the vitriol-chambers; I also supply this water in a finely divided form, and exactly where it is needed for meeting and decomposing the nitrososulphuric acid condensing on the solid surfaces; and by this cooling I protect the apparatus employed against rapid deterioration, such as occurred in the Thyss plan (p. 656).

The apparatus employed is the "plate-column" or "plate-tower," invented by myself and patented in conjunction with the stoneware manufacturer Ludwig Rohrmann (B. Ps. 10355 of 1886; 10037 of 1887; 6989 of 1889). It originally consisted of a column of large stoneware cylinders, filled with the plates forming the peculiarity of the invention; and this is the construction still employed for nitric and hydrochloric acid (p. 164); but for the purpose of sulphuric-acid manufacture it is constructed with a leaden shell, *a*, of either round or angular section, and stoneware plates, *b b*, as shown in Figs. 201 and 202. The plates are supported by bearers, *c c*, in such a way that each plate is independent of the others, and presses only upon the horizontal ledge of its own bearer, whilst the pressure of the superposed plates and bearers is sustained by the vertical part of the bearers. The latter are easily arranged so as to protect the whole inner surface of the lead against the attack of the chemicals and the high temperature ruling within. We do not here notice such parts as the feeding arrangements, inlet- and outlet-pipes, and the like, which require no special explanation; the feeding arrangement will be described in Chapter VI., in connection with the Gay-Lussac tower. A special explanation is only necessary for the plates *b b*. Fig. 203 shows

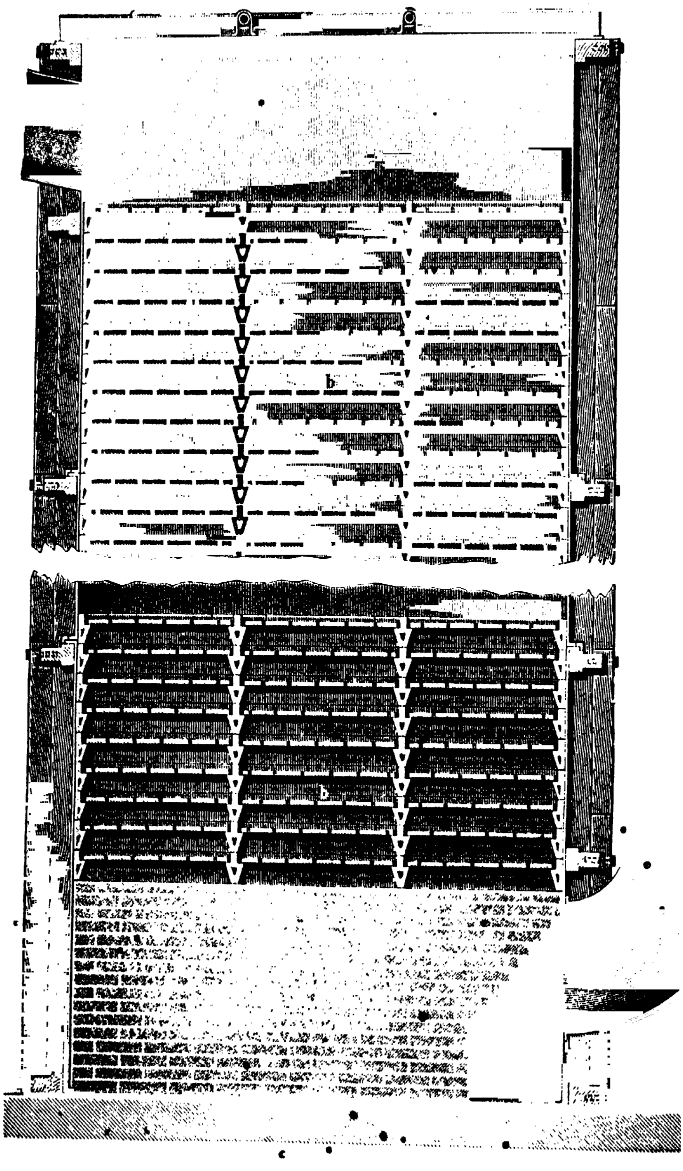


FIG. 201.

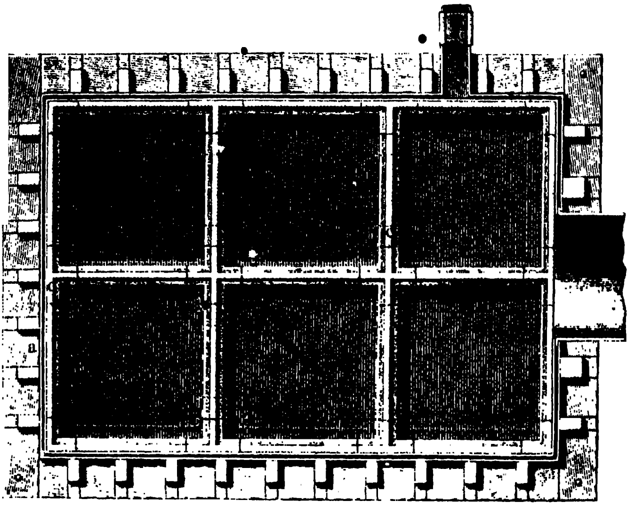


FIG. 202.

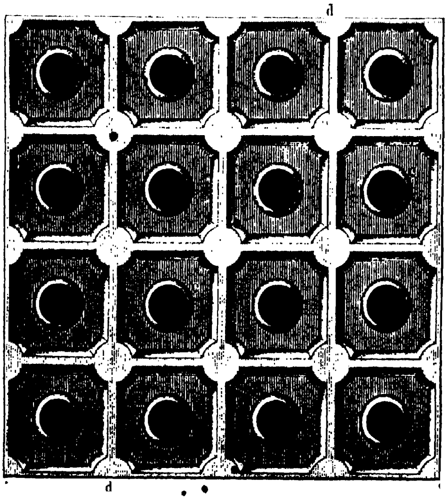


FIG. 203.

a small portion of their surface as seen from the top, Fig. 204 the same as seen from the bottom, Fig. 205 a section of pieces of two superposed plates.

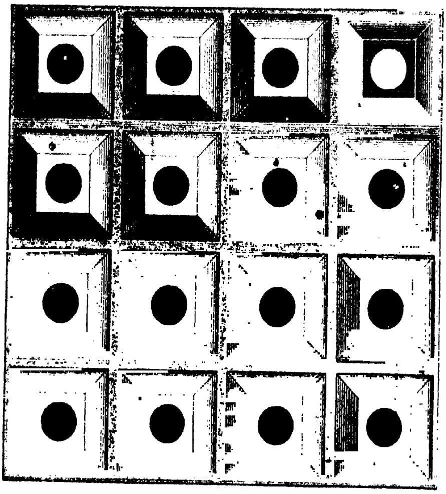


FIG. 204.

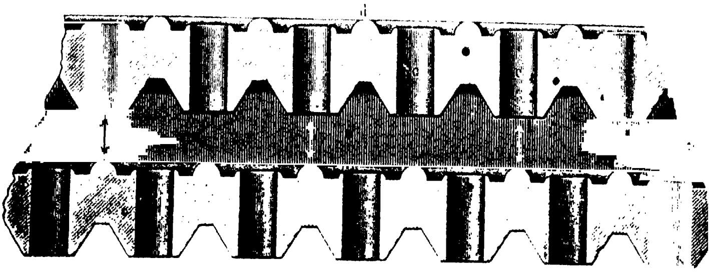


FIG. 205.

Each of these is covered with a network of small ledges, *d d*, and in each of the squares thus formed there is a perforation, *e e*, with a somewhat raised margin. The height of this margin is not quite so great as that of the ledges, hence there is always a layer of liquid about ⅛ in. deep in each of the squares; and as there is always more liquid dropping in, the excess is forced out through the perforations drop by drop. The plates are not identical in shape, but differ as to the position of the holes. To each perforation in any one plate there corresponds the point of union of the ledges in the plates above and below (see Fig. 205). Hence the liquid cannot drop straight through the holes in the following plates, but it strikes the solid portion of the next plate, is scattered about, and is divided among the adjoining squares. This action is repeated from plate to plate. Thus the thin layer of liquid resting upon the plates and clinging to the holes is constantly renewed, and by the scattering about of the liquid another absorbing surface is created.

The gases and vapours rising within the tower pass through the numerous holes of the lowermost plate and are thus divided into a great number of fine jets. Immediately on issuing through the holes of this plate, they strike against the solid places in the next plate above, which correspond to the holes, and are thus divided and again mixed; and this process is repeated as many times as there are plates provided. Whilst the gases and vapours thus travel upwards in continuously renewed mixtures, they come into the most intimate contact with the absorbing-liquid, which they meet within the narrow holes on the plates and scattered all over in fine drops. By the incessant changes in the direction of the current, and the equally incessant renewal of the surface of the liquid, the most favourable conditions are produced for a mutual action of the gaseous and liquid substances. Owing to the principle of the apparatus, no false channels can exist in which the gases or liquids would travel separately without coming into proper contact with each other.

This circumstance partly accounts for the enormous difference in condensing-power between the "plate-tower" and a perfectly well-constructed and packed coke-tower, or any similar apparatus, fitted with pieces of pottery and the like. The liquid within a coke-tower is never quite evenly distributed; there are always many places where it drops down a considerable height without meeting a piece of coke, and where, on the other hand, the gases find channels in which they can ascend without for some time getting mixed and coming into contact with liquid. Moreover, the individual gas-channels are too *wide, and the inner portion of the gaseous current does not enter into reaction with the absorbing-liquid. This is unavoidable,* because the interstices between the pieces of coke are quite irregular, and therefore the section of the tower must be made wide enough and the pieces of coke large enough to secure a sufficiency of draught for the worst case. Nor, as experience has demonstrated, have any arrangements of cylinders, pipes, or other pieces of pottery hitherto had a better effect than coke. Hence coke-towers must be made very wide and high, thus giving a long time and corresponding opportunities for mixing the gases and enabling them to come into contact with the liquid; and in this way the reaction is certainly very complete at the end. But this enormous enlargement of space can be avoided by the systematic way in which, in the plate-tower, the gaseous current is split up into upwards of a thousand very thin and exactly equal jets, which must continually alter their direction, and must therefore become thoroughly mixed each time they pass through a new plate. On their way they come into the most intimate contact with constantly and systematically renewed thin layers of liquid. The network of ledges prevents any unequal downward passage of the liquid, unlike the action of coke-towers or of any other hitherto known form of similar apparatus. Perhaps a still more important difference is the following:—There is a very thin and constantly renewed layer of liquid spread over each plate, and the gases, in passing through the perforations of the plate, must frequently break through the drops of liquid. This seems to produce an action somewhat similar to the Coffey still or other "rectifying" apparatus, and it may to a great extent explain why such an intense action takes place in so small a space.

Owing to these advantages, a plate-tower, in comparison with a coke-tower, does from ten to twenty times as much work in the same cubic space. It can therefore be made not merely much smaller in section, but also much lower in height, and the feeding-liquid requires correspondingly less pumping. A column of 40 plates would be only 18 ft. high. The above is a comparison between plate-towers and coke-towers; the difference between the former and empty chamber-space is much greater, as we shall see.

In our present case it is of special importance that the *injurious action exerted by the reducing power of coke upon he nitrous gases (p. 350) is avoided, the stoneware plates being* absolutely *stable in the chamber atmosphere if manufactured* of proper quality. The plates, therefore, last for ever; even if cracked they may still continue in use.

When a plate-column is partly obstructed by muddy deposits, it is very easily cleaned out by a thorough flushing with water, or, in bad cases, by removing the cover and lifting out one plate after another.

Apart from the great constructive difference between the plate-towers and all previously proposed apparatus, there is an equally great difference in their mode of application. If the tower were left to itself, like Ward's or Thyss's apparatus (pp. 649 and 650), the very completeness of the mixture produced therein would produce an intense chemical reaction, and, consequently, a very injurious development of heat. This is, however, entirely avoided by feeding the towers with a stream of water or dilute sulphuric acid, at such a rate that, by the vaporisation of water, the temperature does not rise above 70° or 80°. The intimate contact between gaseous and liquid particles within the plate-tower must bring out the cooling action of the evaporation of water to its fullest extent, and at the same time the water required for the chemical reactions of the acid-making process is supplied here without any previous production of steam or spray; the superfluous steam passes over into the next chamber and does its work there. The acid running off at the bottom is either used up as it is, or is run into one of the chambers, or it is employed for feeding the Gay-Lussac tower.

In plate-towers there will always be a great excess of nitrous gas and of oxygen; hence there is very little fear that even when employing water for feeding them there will be the conditions present for the formation of nitrous oxide, which would mean a waste of nitre. This can be avoided in any case by feeding the columns with sulphuric acid of 1·3 sp. gr. or upwards, since I have already shown (*Ber.*, 1881, p. 2200; cf. *suprà*, p. 337) that in this case no N_2O whatever is formed. In practice such dilute acid or chamber-acid is employed for feeding the columns.

The principal advantage of this system is that, like the Glover tower, it brings about the mutual action of the ingredients within the smallest possible space. We shall see in Chapter VI. that 1 cub. ft. space in the Glover tower effects the formation of as much acid as at least 180 cub. ft. of ordinary chamber-space; and a similar difference may be looked for between the latter and the plate-towers to be interposed between the chambers.

We will now consider the question whether the thermal effects produced in that system are not excessively large or small. The heat of forming H_2SO_4 from SO_2+O+H_2O is 54,400 calories; to this must be added the heat produced in the formation of ordinary chamber-acid, say of 110° Tw., or H_2SO_4, $3H_2O=11{,}100$ calories; altogether 65,500 calories. This is the heat produced in the formation of a quantity of chamber-acid corresponding to 98 g. of H_2SO_4, and it is very little more than would be required for converting 98 g. of cold water into steam. This quantity of water then would have to be evaporated within the tower in order to absorb all the heat produced in the acid-forming process, on condition that the acid must run out cold at the bottom and that the tower would lose no heat by radiation. But as the former condition is unnecessary, and the latter even impossible to maintain, the quantity of water evaporated will be less than the weight of monohydrate produced, and will probably be very nearly equal to that required for the chamber-process, viz., three-quarters of that amount. Any deficiency of water could, of course, be made up by steam, probably best by means of an injector placed in the outlet-tube from the plate-tower.

As a practical way of applying the new system, I proposed from the first the following plan:—Considering that by far the greatest portion of the acid is made in the first part of the chamber, we cut off the back part altogether, and leave behind the Glover tower a chamber of only about 50 ft. length. Behind this we place a plate-tower of sufficient section for the amount of gas to pass through and 40 plates high (say 18 ft.). Then comes a small chamber, say 30 ft. long, again a plate-tower, a last chamber for drying the gases, and in the end a plate-tower serving as Gay-Lussac tower.

The question might be raised why I did not propose to carry on the whole of the sulphuric-acid-making process in plate-towers or similar apparatus. But a glance at the curves shown in Chapter VII. will show that the first part of the first chamber is really very efficient, and whilst the gases are of such concentration a lead chamber is possibly the cheapest apparatus for making sulphuric acid. As soon as the curves begin to bend towards the horizontal, that is, when the reactions become sluggish, it is time to liven them up by apparatus like the plate-towers. But if such were attempted to be used from the first, the heat would become excessive, which would be very injurious both to the material of the apparatus and to the process. For this reason the process proposed by Hannay (B. P. 12247 of 1886, *cf.* Chapter XII.) is not likely to be practically successful.

The first factory which ventured to try my plate-towers (which have become known as "Lunge towers," both in their application as intermediate "reaction" towers for the vitriol-chambers, and as replacing coke-towers for the recovery of nitrogen acids, for condensing hydrochloric acid, and so forth) was the old-established acid-works at Lukawetz, in Bohemia, soon followed by a factory at Valencia, in Spain, both in 1891, and by others in various countries. Of course here and there difficulties were experienced, principally caused by the obstruction of draught. Thus in *Z. angew. Chem.*, 1895, p. 407, P. W. Hofmann alluded to a trial which failed because the holes in the plates, 8 mm. bore, became filled with liquid and thus stopped the draught. I myself (*ibid.*, p. 409) completely refuted this objection, mentioning that already about 200 plate-towers were then at work, most of them with even smaller holes, and a large number with 8 mm. holes, in sulphuric-acid works. These works had been very successful, as was authentically proved by the replies to interrogations put to certain firms, which also show that, if the section of the tower is sufficiently large, no trouble is caused by draught of the kind mentioned by Hofmann. Since the principle of artificial draught by means of fan-blasts is becoming more and more applied to vitriol-chambers, the complaint against the plate-towers on the above ground is practically meaningless.

The greatest development of the plate-tower system took place when H. H. Niedenführ, chemical engineer of Berlin, took the matter in hand. He designed and started many chamber-plants on that system, and studied all the conditions necessary for success, so that I shall refer principally to him in the following description.

The part played by the Lunge towers in the manufacture of sulphuric acid has been discussed at length by Niedenführ, in *Chem. Zeit.*, 1896, p 31. According to him, plate-towers are not very well adapted for replacing the whole of the ordinary vitriol-chambers; the first part of the process is always best carried out in a single lead chamber, as here the gases are still sufficiently concentrated to react upon each other. [In this view, as well as in all other essential points of Niedenführ's paper, I fully concur.] Here also the flue-dust and the excessive rise of temperature would act injuriously. Hence it is not advantageous to place a Lunge tower between the Glover tower and the first chamber, but it should be placed in the central or back part of the set of chambers. Even then the results obtained with these towers do and must differ at different works, according to circumstances, viz., the available chamber-space, the draught, the size of the burners and of the connecting-pipes, of the Gay-Lussac tower and so forth. In some cases the working-capacity of the tower is partly taken up for correcting some fault in the set of chambers to which it has been applied. Niedenführ quotes the following special instances of the work done by Lunge towers, as personally observed by him in the cases stated.

In one case, a Lunge tower was placed between the two chambers of a set, which were of equal size; the total length of the set was 193 ft. 6 in. and its contents = 94,640 cub. ft. The quantity of Sicilian sulphur burnt previously did not exceed 30 cwt. per twenty-four hours; but after putting up the tower it could be raised to 46 cwt., evidently because the time and the length of the path of the gases had been thereby increased, to such an extent that the set could be worked with stronger draught, and more sulphur could be burnt accordingly. In another case (4 chambers, total capacity 38,150 cub. ft., length 78 ft. 6 in.) the production could be increased from 15 to 18 cwt. of Sicilian sulphur per day. This means that some improvement had been effected, but principally in this respect, that the previously observed fault, viz., the carrying forward of the process into the Gay-Lussac, was now avoided. In a similar case, the production rose from 16 to 19 cwt. of sulphur; in both cases less nitre was consumed than previously. The towers thus spent part of their efficiency in correcting the faults of the old plant, and this in many cases would be a very desirable object; but the quantitative results thus obtained do not represent the whole of the working-capacity of the towers, which in some more favourable cases has admitted of increasing the production by 45 per cent. Nearly in every case observed by Niedenführ this capacity of the towers had not been exhausted, for the chamber following upon the towers had hardly any more work to do; more work could have been done by increasing the number of the burners, by enlarging the connecting-pipes, or by other suitable measures. The very low temperature of the back chambers in this case, however, is useful in condensing part of the nitrous gases and lightening the work of the Gay-Lussac tower. Formerly the acid from the Lunge towers was sometimes too nitrous, but this drawback has been avoided by feeding the towers with acid of from 38° to 42° Bé. (sp. gr. 1·357 to 1·410).

The Lunge tower cannot be simply substituted for a Glover tower, as the holes of the plates would be too quickly stopped up by flue-dust, and in washing this down they would easily crack. Niedenführ, however, recommends placing a few tiers of plates with ½-in. holes in the upper part of the Glover tower. He quotes a case where a Lunge tower was found specially useful in completely denitrating chamber-acid required to be entirely free from nitrogen compounds. [*Cf.* another case of special utility in Chapter VI.]

Especially good results have been obtained in a number of cases, personally observed by Niedenführ, where plate-towers were employed as auxiliaries to Gay-Lussac towers. They act not merely in promoting the absorption of the nitrous gases, but also in rendering the chamber-work much more regular, especially in places where the chambers are subjected to sudden changes of weather, gales, etc.

Niedenführ in the above-quoted paper makes certain proposals for the erection of sulphuric-acid works, forming a combination of chambers and plate-towers, which we do not quote here, because they are rendered obsolete by recent experience, the result of which will be noticed in Chapter X., where a complete plan for this purpose will be given. [*Cf.* also p. 676.]

Lüty (*Z. angew. Chem.*, 1897, p. 484) also discusses at length the function of "Lunge towers" as intermediate reaction-towers.

He quotes the results of ten different works employing such towers between the chambers as means for reducing the chamber-space, from England, Scotland, Spain, Russia, Denmark, showing a large saving of space, without any increase in the consumption of nitre. He also gives detailed estimates showing that, apart from the saving of ground-space, a set of chambers provided with such reaction-towers costs 35 per cent. less than ordinary chambers for the same production.

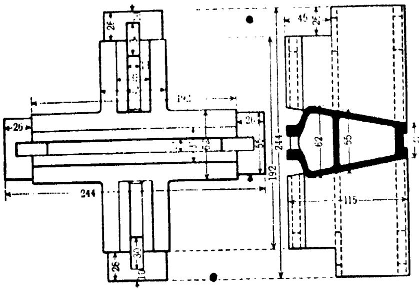
Later on, Niedenführ (*Chem. Zeit.*, 1897, No. 20) quoted practical results from two English works. One of them replaced the last chamber of a set, with a capacity of 38,390 cub. ft., by a Lunge tower of 256 plates in 16 layers, with the same make as before. Here each plate actually made 10·6 kg. H_2SO_4 in twenty-four hours, or 216·7 kg. per cubic metre of the space filled with plates, *e.g.* about one hundred times as much as ordinary lead chambers. Another factory, with very poor gases, still made 88·3 kg. H_2SO_4 per cubic metre of plate-space. [*Cf.* also *Z. angew. Chem.*, 1900, p. 960.]

Niedenführ (private communication) gives the following detailed instructions for the building of Lunge towers, taking, for instance, a tower of a sectional area of 20 plates, 2 ft. square each, placed 4 × 5.

A brick foundation is usually made, but in case of need the tower can be placed on the flooring surrounding the chambers, if properly supported. The leaden shell is erected, with its outer frame of wood and a lead bottom. On this a dwarf wall of 9-in. fire-bricks is placed all round the circumference, and a central supporting pillar. This wall supports an iron frame, consisting of one or more (in this case of six) pieces. The middle pillar supports the places where four of the six pieces meet. The iron frame is covered with lead, the joints being so arranged that the upper, bearing surface remains free and smooth. On this frame the stoneware bearers (Figs. 206-211) are placed. There are corner pieces, *a*, which carry one of the corners of the plates, the three others being supported by T-pieces, *b*, and cross-pieces, *c*. Between these pieces the longitudinal bearers are placed along the lead sides of the tower. In order to prevent any shifting of the pieces, wedges are put in suitable places.

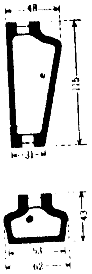
Upon the frames thus prepared the Lunge plates are put,

FIG. 208.



Scale 1:6

FIG. 207.



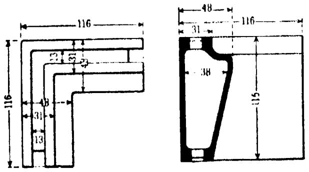


FIG. 206.

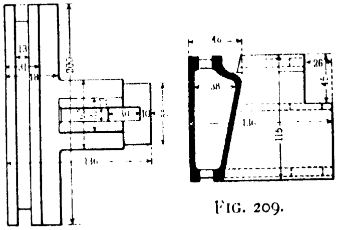


FIG. 209.

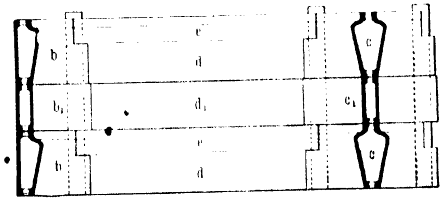


FIG. 210.

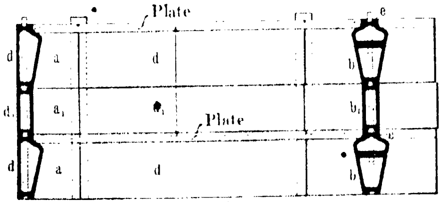


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FIG. 211.

and after finishing off one layer the parts forming the next frame are placed upon the corresponding cross- and angle-pieces, etc. The parts *a*, *b*, *c* are so chosen that there is a distance of $2\frac{1}{2}$ in. between the single layers of plates. If a greater distance is desired, we place below the parts *a*, *b*, *c* other cross-, T-, and angle-pieces, a_1, b_1, c_1, 3·14 in. high. According to the number of layers of bearing-pieces we designate the distance from plate to plate as single, double, treble, etc. The tower in question has in its lower part 10 layers at single distances and 6 layers with double distances.

The top of the tower is made of lead, and is provided with a proper feeding arrangement.

If plate-towers are to be combined with existing systems, it is of course necessary to consider the place and level where the towers are to be erected, and their dimensions, in connection with the existing circumstances, so that it is difficult to lay down general rules. But where new plant is to be erected, long experience now admits of establishing certain rules.

It is possible (as Mr Niedenführ later on proposed) to replace the lead chambers altogether by Lunge towers, by taking care to erect the first part with as little loss of draught as possible, and to remove the heat of reaction to the necessary extent. This is done by making the reaction-towers, immediately following the Glover towers, of a wider section, and providing them with a very efficient feeding arrangement. The last towers must be made narrower than corresponds to the volume of gases passing through the first towers, so as to exert a certain pressure on the gases which promotes the reaction. The plate distances in these final towers must be kept smaller than in the first towers.

The horizontal sections of Lunge towers may be chosen according to the following particulars:—

Sulphur to be burnt per twenty-four hours.	Number of plates to be employed per ton of sulphur burnt in twenty-four hours to replace the chambers in different parts of the system—		
	In front.	In the middle.	In the rear.
Up to 1 ton S . .	12	10	6
From 1 to $2\frac{1}{2}$ tons S .	12 to 10	10 to 8	6 to 5
From $2\frac{1}{2}$ to 5 tons S .	10 to 6	8 to 5	5 to 4

The number of layers for a given production is calculated as follows:—In the first third of a system, where the plates are at a treble distance from each other, each plate may be assumed to produce in twenty-four hours from 10 to 12 kg. H_2SO_4; in the second third, with double distances, each plate = 6 to 8 kg. H_2SO_4, in the last third, with single distances, 1·25 to 2 kg. H_2SO_4.

Just as it is irrational to make a chamber-system of one chamber only, which favours the diffusion of the inactive residual gases with the active ones, it would be wrong to try manufacturing with one tower only, instead of dividing the work over several towers.

Mr Niedenführ believes the following arrangement to be suitable for working with towers alone, without chambers (Figs. 212 and 213). The burner-gases pass through *a* into

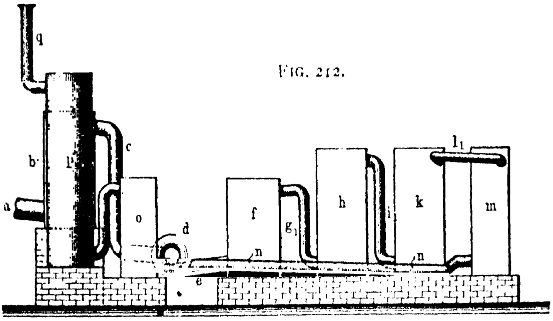


FIG. 212.

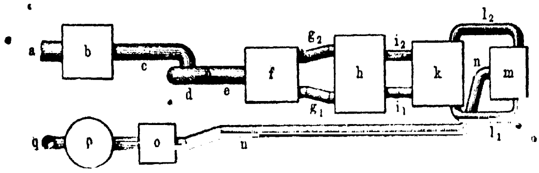


FIG. 213.

a preliminary tower *b*, and through *c* into the fan-blast *d*, which conveys them through *e* to the denitrator *f*. This apparatus is fed with nitrous vitriol and warm water or dilute acid so as to furnish acid of 54° Bé. (= 119½° Tw.). It also receives the nitric acid required for making up the losses. It is packed like a Glover tower, preferably with dish-like packing. Part of the acid here made is employed for feeding tower *b*. This denitrating tower is constructed on the same principle as Niedenführ's ordinary Glover towers (*cf.* next Chapter), viz., with an interruption of the packing intended to facilitate the cleaning of the bottom part, and with sufficiently large openings for the passage of the gas. In tower *b* the acid with which it is fed is concentrated, the gases are purified and partly cooled so that they may pass through the fan-blast without any trouble. They effect the denitration in *f* and then pass through g_1, g_2, to the first plate-tower *h*; pipes g_1, g_2, as well as the further pipes i_1, i_2, are provided with steam-pipes. Tower *h* is filled with 12 layers of 24 plates each in treble distances; tower *k* with 18 layers of 20 plates each in double distances. In *h* and *k* the gases enter at the bottom and issue at the top; but in the last reaction-tower *m* they enter at the top and leave it at the bottom through *n*, which arrangement has been found to give the best result. Tower *m* contains 30 layers of 12 plates each in single distances. The gases now pass into the first Gay-Lussac tower *o*, containing 16 layers of 9 plates each, then into the second Gay-Lussac *p*, packed with coke, and finally through *q* into the open air.

The acid coming from the first Glover tower, *b*, is freed from most of its impurities by means of an air-cooler.

The just-described system would serve to treat the gases from 2500 kg. = 2½ tons sulphur per diem. The production of acid would be divided as follows:—

Tower *h*, 288	plates at	10	kg. H_2SO_4	=	3168	kg.	H_2SO_4.
„ *k*, 360	„ „	7	„ „	=	2520	„	„
„ *m*, 360	„ „	1·75	„ „	=	630	„	„
Glover and Gay-Lussac Towers	.		.		882	„	„
Total	.		.	.	7200	„	„

If the same production is to be attained by means of a combination of chambers and plate-towers, this can be done as shown in Figs. 214 and 215.

From the Glover tower, *a*, the gases pass into a lead chamber, *b*, containing 1064 cb.m. = about 38,000 cub. ft., provided with air-cooling shafts, c_1, c_2, c_3 (*cf.* p. 653). In this case no fan-blast need be employed, but the gases must have a sufficient upward draught from the burners to the Glover tower and from this to the chamber *b*. Now come the two plate-towers *d* and *e*. These, as well as tower *a*, may be placed at a lower level, which is all the better for the work. The Lunge tower *d* contains 20 layers of 20 plates each in double distances, tower *e* 30 layers of 12 plates each in single distances. At *e* the gases are passed in at the bottom and out at the top, and then through *f* into the first Gay-Lussac tower (a plate-tower) *g*, into the coke-packed Gay-Lussac *h*, and through *i* into the open air. The production will be approximately divided as follows:—

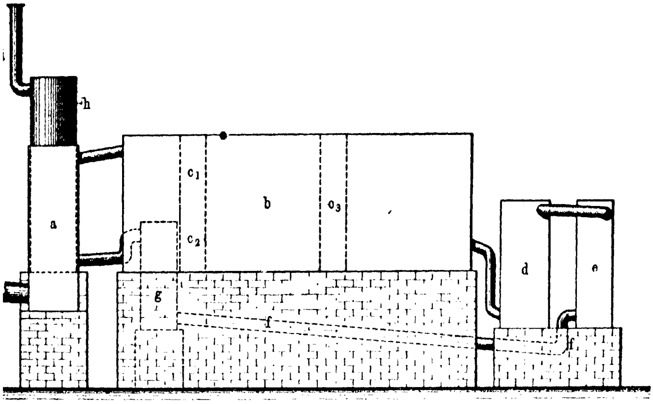


FIG. 214.

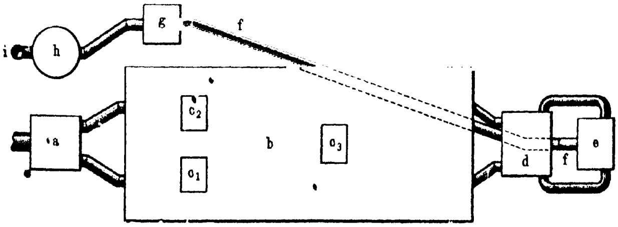


FIG. 215.

Chamber *b*, 1024 cb.m. at 2·75 kg.	. =	2926 kg. H_2SO_4.
Tower *d*, 400 plates at 7 kg. .	. =	2800 ,, ,,
,, *e*, 360 ,, at 1·15 kg.	. =	630 ,, ,,
Glover and Gay-Lussac Towers	.	844 ,, ,,
Total . .		7200 ,, ,,

In a similar way larger systems can be constructed with one chamber and a suitable number of Lunge towers. Mr Niedenführ would not even for the largest systems propose more than two chambers, placing between them a very wide plate-tower with great distances, and behind the second chamber all the remaining towers. In Chapter X. complete plans will be given for such a combination.

In order to apply the Lunge towers to existing systems, for the purpose of increasing the production, the circumstances of each case must be critically considered in the light of the large experience now gained. It will usually be best to place the towers behind the last chamber. The horizontal section of the towers can be calculated from the last column of the table given on p. 677; in the case of very large systems from the second and the last column; with good draught the plates should be kept at single or double distances.

If, however, plate-towers are to be placed *between* existing chambers, all the conditions of the system must be carefully considered according to the experience gained therewith. Above all, the towers in large systems should not be arranged just after the front chamber, but between the back chambers. The horizontal sections, the places in the system, etc., must be calculated according to the general instructions given above. If we were, for instance, to place a Lunge tower between No. I. and No. II. in a system of four chambers, the last three chambers would do very little work. It will be much better to place the tower between Nos. III. and IV. or behind No. IV.

Mr Niedenführ thinks that, in view of the considerable saving of expense effected by these improvements of the ordinary chamber-process, the contact systems cannot compete with the former in the production of acid up to 142° Tw., and their superiority comes in only for acids above that strength.

A very instructive plant was erected by Mr Niedenführ at the "Lazyhütte" works. The chamber-system consisted originally of four chambers, with a total capacity of 7110 cb.m. (=250,000 cub. ft.), and three Glover towers, two of which were always working at the same time. In 1900, working with zinc-blende and "forced style" (p. 639), this set produced on an average 25,580 kg. acid of 50° Bé. (106° Tw.) per twenty-four hours, with a consumption of 3·03 nitric acid 36° Bé. per cent. sulphuric acid. In 1901 four Lunge towers were erected behind the last chamber, viz.: No. I. 12 layers at 20 plates, double distances; No. II. 16 layers at 20 plates, partly single, partly double distances; No. III. 25 layers at 16 plates, single distances; No. IV. (acting as a first Gay-Lussac tower) 18 layers at 25 plates, single distances. The production now rose to 36,458 kg. acid of 50° Bé., consuming 1·90 per cent. nitric acid 36° Bé. per cent. sulphuric acid. Evidently the plant was not working up to its full capacity, but as there was not enough draught, a fan-blast was placed behind tower No. IV. The production of acid rose at once, but during a few days also the consumption of nitric acid (to 4·76 acid 36° Bé. per cent.). When, by a number of tests, the draught had been properly regulated (although not to the fullest possible extent, since there was only a temporary source of power for the fan-blast, to be replaced by a better engine at the first opportunity), the production rose permanently to 44,600 kg. acid of 50° Bé., with a consumption of only 1·7 per cent. nitric acid 36° Bé. This, for Upper Silesian zinc-ores, is a most excellent result, both as to production of acid and saving of nitre.

Place where the observations were made.	Before applying the fan-blast (September and October).		After applying the fan-blast (November and December).			
			Before properly regulating the draught.		After thoroughly regulating the draught.	
	Pressure mm. water.	°C.	Pressure mm. water.	°C.	Pressure mm. water.	°C.
Gas-pipe between—						
Ch. I. and II.	+ 1·6	90	+ 1·0	104	+ 1·9	91
Ch. II. and III.	+ 1·1	69	+ 0·2	86	+ 0·5	73·5
Ch. III. and IV.	+ 0·75	54	- 1·0	...	- 0·5	65
Ch. IV. and Tower I.	+ 0·6	...	- 3·8	...	- 4·3	...
Tower I. and II.	0·9	...	- 5·0	...	- 5·8	...
Tower II. and III.	- 1·6	...	- 6·2	...	- 7·4	...
Tower III. and Gay-Lussac (IV.)	3·6	38	+ 7·4	...	+ 7·4	30
Tower IV. and Coke-tower (Gay-Lussac)	4·5	...	+ 4·8	...	+ 4·0	...
Coke Gay-Lussac and chimney	- 9·4	...	1·4	...	- 5·0	...

The above estimations of temperature and manometric pressure, made with this system, after the erection of the plate-towers, at three specified times (viz., before and after the increase of draught by means of the fan-blast), are quoted here for the sake of indicating their connection with the above-mentioned alterations, but we shall later on describe the regulation of temperature and draught of chamber-systems.

Other Apparatus on the Principle of Plate-towers.—After the success of the principle embodied in the "plate-towers" had been thoroughly established, it was only natural that other inventors should try, more or less successfully, to attain the same end by other means, not coming under the Lunge-Rohrmann patents. This was all the more likely, as the price of the "plates" and the fittings belonging to them was at first rather high, owing to the technical difficulties of their manufacture. Since these difficulties have been entirely overcome, the price of the plates, etc., has been so very much reduced that most of the imitations have lost even any advantage in respect of first cost, apart from their inferior efficiency. I shall, however, quote all the more important of these imitations.

One of the objects aimed at by some of the inventions concerned is to avoid any impediment to the draught, for which the plate-towers are sometimes blamed. As we have seen (p. 677), this objection is of no account in view of the ease with which the chamber-draught can be regulated by fan-blasts, and it should be borne in mind that the efficiency of an apparatus of this kind is practically proportionate precisely to its draught-impeding capacity.

Hacker and Gilchrist (B. P. 15895 of 1893) employ the same principle that I have adopted in the "plate-towers," to which they expressly refer. Instead of my geometrically constructed stoneware plates for dividing the gases, the liquid acid, and the acid vapour, they use a number of horizontal lead tubes, running from one side of the tower to the other and alternating in position. These towers, which they call "pipe-towers," are fed with water or sulphuric acid; cold air is drawn or blown through the pipes. A paper in *J. Soc. Chem. Ind.*, 1894, p. 1142, contains a detailed account of this system, in discussing which several speakers threw great doubt upon its efficiency. This is hardly just, as the introduction of these "pipe-towers" into many American factories seems to show. They cannot possibly do as much work as "plate-columns" of the same size, but undoubtedly they are of some use. Another paper on these towers was published in *J. Soc. Chem. Ind.*, 1899, p. 461, containing some improvements in details. The success of this system as intermediate towers between the chambers is the best proof of the correctness of the principles which led me to the construction and application of the "plate-columns," of which the "pipe-towers" are an imperfect imitation, made of a material liable to corrosion instead of indestructible stoneware. A similar plan is that of Winsloe and Hart (B. P. 20142 of 1901), who employ perpendicular air-cooling pipes in a shaft connecting two chambers.

Hart and Bailey (*J. Soc. Chem. Ind.*, 1903, p. 473) describe a plan exactly similar to Hacker and Gilchrist's pipe-towers, only of somewhat larger dimensions. They found a cooling-action of nearly 40° C., an increase of production of 60 per cent., and a decrease of nitre of from 3·5 down to almost 2·0 per cent. All this agrees perfectly with the views first clearly stated by the author of this book. The acid scrubbed out in their pipe-towers contained practically no nitre. [They state the strength of this acid to vary between 90° and 120° Tw., but they do not distinguish between the reactions shown by the lower and the higher of these strengths. While at the lower strength no "nitre" could be retained, it is inconceivable that acid of 120° Tw., condensed from the vesicular to the completely liquid state in an atmosphere of nitrous fumes, should not contain any nitre !]

Rabe (*Z. angew. Chem.*, 1903, p. 437) makes general observations on the principles on which towers are constructed. He also describes a feeding-arrangement with automatic movement and arrangements for internal cooling of such towers.

Benker (Fr. P. 238872) places between the chambers leaden towers, 5 ft. wide and 20 or 25 ft. high, fitted with earthenware cylinders 4 in. wide and 3 to 4 in. high. These are fed with nitrous vitriol from the Gay-Lussac towers at the top, and with a steam-jet at the bottom. The strength of the out-flowing acid is maintained between 112° and 123° Tw.; it is kept a little nitrous, to avoid the reduction going too far. Such a tower is placed behind the first chamber, which is made large enough to consume all the steam coming from the Glover tower; another tower is placed between the second and third chambers.—This is, of course, a simple imitation of Lunge towers by cheap, but imperfect means.

Guttmann (Ger. P. 91815) recommends as a "packing" for reaction-towers perforated globular bodies made of earthenware, glass, or metal. As shown in Fig. 216, the perforations are continued into short pipes turning into the inside of the globe. These bodies may also be undulated inside and outside, to increase the acting surface. They can be put into the tower without any special care in packing. The liquid runs down both inside and outside, and the gases are well mixed.

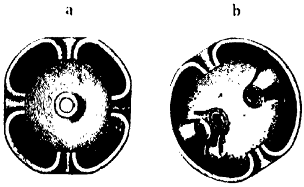


FIG. 216.

Niedenführ objects to hollow balls on the system of Guttmann and others, because, firstly, most of the perforations get closed up when filling the tower; secondly, the gases are sure to take the easier way round the balls, instead of forcing their way with increased friction into the interior, and whatever does enter the balls will remain there for an indefinite time without taking part in the reactions.

Heinz (*Z. angew. Chem.*, 1906, p. 705) considers Guttmann's globes to be the best possible packing for Gay-Lussac and for the upper part of the Glover (in the lower part of the Glover they are too quickly stopped up by mud); also for intermediate towers. According to his calculations they cost only one-fifth of "plates," and a Guttmann tower costs less than half of a coke-tower of equal duty.

Lunge (*ibid.*, p. 1125) controverts the calculations of Heinz, which are made entirely on paper, without any regard to the complicated conditions ruling in practice.

Another kind of reaction-apparatus consists of the '*Kegeltürme*' (cone-towers) of the Bettenhausen ceramic works. They are filled with slightly conical bodies, open at the bottom and provided with a shallow basin at the top. Niedenführ (*Chem. Zeit.*, 1897, No. 20) says that they are much less active in dividing the gas than Lunge plates (only from 14 to 138 times per square metre, against 2400 times in the case of Lunge plates), that they contain less than half the acid-covered surface, and that the hollow space is altogether a mistake, since the gases will stagnate in them. Lüty (*eod. loc.*) also criticises the

Bettenhausen cones adversely. We shall refer to them again in the next and also in Chapter XII., in connection with the Gay-Lussac and Glover towers.

Cellarius (Ger. P. 166745), with the special object of separating the sulphuric acid already formed from the chamber-gases, places between the first and second chamber a leaden tower, packed with coke, in which a vortex is produced by means of a fan placed in the tower and set into motion by a jet of steam. The same object is aimed at in his B. P. 22080 of 1905, and his Fr. P. 360634. In Ger. P. 183097 he improves that process by employing two concentric cylinders, connected by horizontal perforated partitions, through which the gases are propelled and where they meet the condensed acid flowing down. They are thus purified from acid-fog and dust.

Schwab and H. Greene & Sons (B. P. 24619 of 1903) employ mixing-towers, communicating with the chamber at top and bottom. By means of steam jets and the way of arranging the inlet of gases the pressure in the upper part of the tower is decreased, so that the circulation of the gases is promoted. In long chambers one or more vertical shafts are arranged, with a steam jet, discharging horizontally at the lower end of the shaft, towards the outlet end of the chamber.

Olga Niedenführ (Ger. Ps. 189238 and 189330) employs reaction towers or chambers, in which the gases travel from the top downwards parallel to the feeding-liquid, which keeps them a longer time in the sphere of reaction. The entrance openings for the gases are arranged in the centre, or symmetrically in the top of the reaction space, and the exit openings in a similar way.

The same inventor (Ger. P. 189834) describes a round acid chamber in which spiral diaphragms are arranged. The gases are conducted either from the centre outwards, or in the opposite direction, in a spiral course. The spiral diaphragms are built of perforated bricks, preferably in the shape of "Meissen" dishes, which are separated by a horizontal diaphragm into an upper and lower part.

The same (Ger. P. 200820) proposes placing a certain number of *small* chambers in the centre, and the Glover, Gay-Lussac, and reaction towers in an outer circle. The gases may be first passed through the towers and then into the centrally-placed chambers. The velocity of the gases is thus lessened in the central part and increased outside, and a thorough mixture is effected. The inner portion is less cooled by radiation, and a very intense reaction takes place there.

Brandenburg (B. P. 7116 of 1907) describes apparatus in which the gases are kept in suspension by centrifugal force in order to reduce the pressure against the rising gases.

Wilhelmi (Ger. P. 184842) describes towers, very similar in principle to the plate-towers (*Z. angew. Chem.*, 1911, pp. 975 to 978).

Lihme and the Grasselli Chemical Co. (Amer. P. 852390) in lieu of intermediate towers, place between the chambers horizontal lead flues, with a large number of lead pipes, open at top and bottom, passed through them in a vertical position, each row being separated by vertical grids from the other. The ascending current of air cools the gases and vapours passing through the flue, and a strong formation of sulphuric acid takes place on the walls of the pipes placed within.

The B. P. of Graham (6051 of 1902) comes just to the same thing. The same inventor (B. P. 10814 of 1906) patents columns with cross-pieces of glass and earthenware, baffle plates, etc, in lieu of coke packing.

Moscicki (Ger. P. 236385) prescribes working reaction-towers in such manner that a large quantity of liquid, say from 6 to 12 per cent. of the cubical contents of the space filled with packing, is run in at once, so that the packing is intermediately completely covered by it and thoroughly washed. His Ger. P. 234259 describes apparatus consisting of three concentric spaces; the central space serves for introducing the gases, the second space is filled with the packing, and the outer space serves for the collection of the gases and vapours after the reaction has taken place.

Jos. Broome holds the Amer. P. 850517 for a special kind of reaction-tower.

Feigensohn (*Chem. Zeit.*, 1906, p. 851) recommends as intermediate towers round lead towers packed with stoneware rings; in front of the Gay-Lussac towers there should be a gas-cooler, made of undulated sheet lead, and behind them Lunge's plate-towers.

Compare also in Chapter VI. the descriptions of packing for Glover towers, partly designed, especially also for the "reaction-towers" here treated.

Replacing the Lead-chambers entirely by other Apparatus, Towers, etc., retaining the Oxidation of Sulphur-dioxide by Nitrogen Oxides.

After all that has been stated on the possibility of carrying out the manufacture of sulphuric acid by the ordinary reaction where nitrous gases are the oxygen carriers, but in a much smaller space than it is done in lead-chambers, the question naturally arises whether the lead-chambers cannot be *completely* replaced by apparatus of greatly reduced cubic space. We have already more than once mentioned proposals in that direction, especially on p. 672, which were caused by the success of the plate-towers. But long before this, inventors had attempted to abolish the lead-chambers. We now enumerate the proposals made in this direction in former and in recent times.

MacDougal and Rawson (B. P. of 21st November 1848) conduct sulphur dioxide and air through nitric acid contained in a Woulfe's bottle, in which sulphuric acid and nitrogen peroxide are generated; the latter, with the air in excess, passes through several vessels filled with water, in which the nitric acid is regenerated.

Hunt (B. P. of 16th August 1853) conveys a mixture of sulphur dioxide and air through a tower filled with pebbles, in which nitrous vitriol continuously trickles down. This principle had already been proposed by Gay-Lussac; and it is actually carried out in the Glover towers, so far as it is practicable—that is, by conducting the escaping gases into lead-chambers.

Persoz (*Technologiste*, xvii. p. 461; *Dingl. polyt. J.*, cxxxix. p. 427; Wagner's *Jahresber.*, 1856, p. 54) passes sulphur dioxide through nitric acid diluted with from 4 to 6 vols. of water, and heated to 100° C., or through a mixture of nitric acid or a nitrate with hydrochloric acid, in a comparatively small glass or stoneware vessel, promoting contact by an agitator. The gases generated by the reduction of the nitric acid ascend in condensing-towers, where they are regenerated into nitric acid by an ascending current of air and a descending jet of water. The sulphur dioxide might even be diluted with carbonic acid, nitrogen, or other gases. In theory this process is right enough; in practice it is said to have failed, principally from the difficulty of constructing vessels suitable for resisting the acids (?).

Verstraet's tubular apparatus (*Bull. Soc. d'Encouragement*, 1865, p. 531; *Dingl. polyt. J.*, clxxix. p. 63; Wagner's *Jahresber.*, 1865, p. 226) has been mentioned previously (p. 652). The Jury Report of 1851 asserted that similar stoneware vessels, constructed by Fouché-Lepelletier, were at work at Javel, near Paris, and that in that factory one-third of the annual make of 3600 tons was produced in them, with one-third of the cubic contents and at one-eighth of the cost of lead-chambers. This assertion has been proved to be entirely erroneous by original correspondence in Hofmann's *Report by the Juries*, 1862, p. 8.

Lardani's apparatus (*Bull. Soc. Chim.*, viii. p. 295; *Chem. News*, 1868, No. 441, p. 238) has also been described above (p. 652); it exemplifies no essentially novel principle.

Kuhlmann (B. P. of 11th December 1850) proposed to force a mixture of sulphuretted hydrogen (from soda-waste) and air through nitric acid, by which nearly all the sulphur was said to be oxidised to sulphuric acid; this is, however, not the case.

Petrie (B. P. of 11th August 1860) employs a system of stoneware pipes filled with pebbles, through which a current of nitric acid passes from one side, and a current of SO_2 and air from the other, the quantities of the materials and the construction of the apparatus being arranged in such a manner as to avoid any loss of nitric acid.

Finch and W. J. and S. Willoughby (B. P. 3086 of 1884) pump a mixture of burner-gases, nitrous fumes, and steam into a tower, where they are subjected to a certain amount of pressure, in order to facilitate their combination. The escaping gases pass forward into other similar towers, and at last through a Gay-Lussac column.

W. Burns (B. P. 14441 of 1886) also seeks to promote the combination of the gases by pressure, together with a peculiar kind of agitation, in an ingeniously devised, but hardly practicable apparatus.

Hannay (B. P. 12247 of 1886) passes the sulphurous and nitrous gases through a condensing-tower, where they become minutely subdivided and thoroughly mixed by passing through screens, which are kept moistened by a continual stream of water trickling on them, the process being repeated until the solution of sulphuric acid formed acquires sufficient strength, when it is drawn off and a fresh supply of water is run into the apparatus.

A. and L. Q. Brin (B. P. 12070 of 1886) burn pyrites with pure oxygen, and convert the mixture of SO_2 and O into sulphuric acid by means of nitrous fumes. A special apparatus for this purpose is contained in my own B. P. 3166 of 1888, which, however, was only taken to cover the ground, the principal object of my invention being the production of sulphuric anhydride, for which, as it then appeared, the cost of pure oxygen might be more easily afforded than for ordinary sulphuric acid.

Durand, Huguenin, & Co. (Fr. P. 205589 of 9th May 1890) pass a mixture of sulphur dioxide and air through tanks, charged with nitric acid or solutions of nitrous products, alternating with condensing-towers. The liquids are made to flow systematically through the apparatus in such a manner that at last concentrated sulphuric acid, free from nitric or nitrous acid, is obtained. The above-mentioned gaseous mixture is produced by passing compressed air into sulphur- or pyrites-burners, thus also obtaining the pressure necessary for forcing the gas through the liquids contained in the tanks.

Barbier's apparatus for manufacturing sulphuric acid (B. P. 12726 of 1892; Ger. P. 69501) consists of six towers, arranged in steps, packed with hollow pieces of sandstone, quartz, or the like. Burner-gas enters the bottom tower and passes through them all. The towers are connected alternately at top and bottom; the last serves as a Gay-Lussac. Nitrous vapours and steam are introduced from a concentrating-pan fired from without. The acid formed in the towers drops into concentrating-pans placed below their open bottoms, or into a collecting-vessel. They are fed with a mixture of sulphuric and nitric acid, if necessary also with steam. Private reports concerning Barbier's apparatus complain of an excessive consumption of nitric acid and also obstructions. The high royalty also acted as a check upon experiments with it. Candiani (*Chem. Ind.*, 1895, p. 153) remarks that the only Italian factory which had introduced Barbier's process (Villafranca) had not been very successful with it. Boissieu (*Bull. Soc. Chim.* (3), xi. p. 726) asserts that the Barbier system has answered very well, but he unfortunately does not quote any figures or other proofs for this assertion; Pierron (*Monit. Scient.*, 1900, p. 367) reports authentically that it has been entirely abandoned.

Staub (B. P. 12675 of 1894) describes a set of five towers, packed with specially moulded earthenware pieces, and fed with nitric acid, nitrous vitriol, etc. Staub's apparatus does not differ in any essential point from the principle of making sulphuric acid by towers alone, without lead-chambers, as attempted by a number of inventors before him. His strange contention that he was entitled to a patent for that *principle*, because he had been the first to carry it out by a special apparatus, was rejected by the German Imperial Court and his Ger. P. 88784 cancelled. Moreover, that apparatus which he had set up in 1895 at Stolberg and in 1896 at Wittenberg was worked only during a very short time, and then stopped on account of bad results and of extremely high consumption of nitre.

Hartmann (*Z. angew. Chem.*, 1911, p. 2303) confirms this from his own observation. The temperature of the towers was much too high; the consumption of nitre came up to 10 to 14 lb. acid of 36° Bé. per 100 chamber acid, and the dark red colour of the chimney gases testified to the escape of nitrogen oxides.

M. Neumann (Ger. P. 169729) makes sulphuric acid in a series of towers, like Glover towers, fed with nitrous sulphuric acid, containing a cooling-zone in the upper part and a heating-zone in the lower part, the temperature being made to rise as the percentage of SO_2 decreases. This process is claimed to effect a considerable saving of reaction space and of nitre.

Heinz and Chase (Amer. P. 875909) pass the burner-gases first through a Glover tower, then through flues, where steam and nitric acid are admitted and part of the sulphuric acid is made; after drying and purifying, the gases pass through a contact apparatus and then through a Gay-Lussac tower.

Rahtjen brings gases containing SO_2, nitrogen oxides, and water in the shape of steam or spray to mutual action in closed spaces at temperatures considerably above 100°, so regulated that the acid produced contains at least 78 per cent., preferably 98 per cent. H_2SO_4. The apparatus consists of iron, lined with acid-proof material.

The Chemische Fabrik Griesheim-Elektron (Ger. P. 226610) have found that the chambers can be entirely replaced by towers, provided that there is such an oxidation of SO_2 that none of it can get into the nitre-recovery towers, which is brought about by introducing an excess of nitric acid. Differently from other tower systems, the formation of sulphuric acid is locally separated from that of nitric acid. It has also been found that the complete oxidation of nitrogen oxides to HNO_3 requires a certain time, on account of the great dilution with inert gases; at least four minutes, so that a pyrites-burner of a capacity of 10 tons and yielding 40 cb.m. burner-gases per minute must be furnished with a nitre-recovery apparatus of at least 160 cb.m. capacity. This system is carried out as follows:—The pyrites-burner gases pass first through a Glover tower and then into the oxidising towers, fed with nitric acid 30° to 35° Bé., where the SO_2 is almost instantaneously oxidised. From the towers runs an acid containing 50 to 54 per cent. H_2SO_4 and about 1 per cent. HNO_3, which is brought back to the Glover for complete denitration and concentration. From the oxidising-towers the gases pass through several towers, fed with mixtures of nitric and sulphuric acid of various concentration, and here nitric acid of a quality suitable for the process is recovered. For working up the SO_2 from burners charged with 10 tons pyrites only 200 cb.m. of total reaction space is required, viz., 30 cb.m. for the oxidation of the SO_2 and 170 for the recovery of the nitric acid. Their additional Ger. P. 229565 prescribes working at temperatures of 35° to 65°. Above 65° part of the nitric acid distils off without having acted as oxidiser, and below 35° the reaction goes on too slowly. This regulation of temperature is most easily attained by employing acid of about 50° for feeding the oxidising towers. Their B. Ps. are Nos. 20401 and 23442 of 1909; Belg. Ps. 218994 and 219727; Fr. P. 406641 and addition; Ital. P. 37914; Austr. Ps. appl. A 66331 and 74991; Norw. Ps. 20774 and 25381; Swed. Ps. 29988 and 30825; Spain Ps. 46267 and 46459; Austral. P. 17739; applications made in Russia and the United States. The process is actually working at Griesheim. Special advantages of it are: that the concentration of the SO_2 gases need not (as is the case in both the chamber- and the contact-process) be confined to very narrow limits, but may vary within very wide limits; that acids of higher concentration than is possible with the chamber-system are obtained; and that the nitric acid employed is recovered as such, which means as the highest and most active oxygen compound of nitrogen. According to Hasenclever (Hurter Memorial Lecture, 25th October 1911; *J. Soc. Chem. Ind.*, 1911, p. 1292) the Griesheim process at that time had not yet reached such a stage of development as to allow a definite opinion upon it to be formed (*cf.* below on the Opl system).

The Erste Oesterreichische Sodafabrik at Hruschau and C. Opl (B. P. 20171 of 1908; Fr. P. 394739; Ger. P. 217036) describe an arrangement for producing sulphuric acid without chambers, on which Opl reports in *Z. angew. Chem.*, 1909, pp. 1961 *et seq.* He started on the well-known theory that the chamber process for producing sulphuric acid may be considered as a contact process in which nitrososulphuric acid acts as catalyser for the combination of SO_2, O, and H_2O. On testing this theory by a set of three washing-bottles, two of which were charged with nitrous vitriol, and the third with sulphuric acid of 60° Bé., and through which pyrites-burner gases, that is SO_2 + excess of O (and N), were conducted, it was found that, on effecting the passage slowly, all the SO_2 was oxidised and retained, and only the excess of O and all N went away. After a certain time, the nitrous vitriol in the first bottle was completely denitrated, and the third bottle contained newly-formed nitrous vitriol. By taking out the contents of the first bottle, putting in those of the third bottle, and recharging this with the acid taken out of the first bottle, the process could be started again. On a large scale this might be carried out in iron or leaden vessels, and Opl calculated that in such vessels, arranged like those employed in Chance's sulphur-recovery process (Vol. II., pp. 943 *et seq.*), 1 cb.m. of nitrous vitriol would produce as much sulphuric acid as 100 cb.m. of chamber space. But on the large scale that system would suffer under the drawback that the burner-gases would have to be compressed and forced through the nitrous vitriol, which would require an excessive amount of moving-power. If, however, the system is carried out in "reaction towers," ten times the size of the wash-bottles will suffice, with much less expenditure of moving power for the gases and for pumping the acid on the top of the towers. And if the acid is raised by "emulsioners" on the system of Laurent, worked partly with compressed pyrites-burner gases, part of the SO_2 is already oxidised in the emulsioners, and the output of sulphuric acid is still greater. The first experimental plant according to this system, erected at Hruschau (Austrian Silesia), consisted of five towers, composed of stoneware pipes 33 in. wide, 10 ft. high. These towers were first left empty, but it was soon found necessary to provide them with suitable packing. The second test was made with the Glover and Gay-Lussac towers of an old chamber set, to which two new towers were added. This set had then (in September 1909) been at work for two years, working up 6 tons of Schmöllnitz pyrites per diem and producing 7 tons, 16 cwt. of acid of 66° Bé., in the shape of acid of 60° Bé, with a daily consumption of 70 to 90 kg. nitric acid 36° Bé. This system has a reaction space of about 250 cb.m., *i.e.*, about one-tenth of the chamber space required for the same production. A new system of six towers, for twice the duty of the old, with many improvements, was then in course of erection. The cost of plant is much less than that of acid chambers; the expense of circulating the acid and cooling-water is slightly greater, but the consumption of nitre is less and all the acid is at once obtained at a strength of 60° Bé. (= 142° Tw.). In the discussion following the reading of this paper, Petersen spoke of the excessively great amount of moving power required by this system, but Raschig was more sanguine and considered it to be that of the future. In 1911 Nemes (*Z. angew. Chem.*, 1911, p. 391) states that the average production of the Hruschau system was 25 kg. H_2SO_4 per cubic metre reacting-space, the consumption of nitre 0·68 per cent. of the H_2SO_4, and that of power 15 h.p., which cannot be called excessive. Hartmann (*ibid.*, p. 2303) makes detailed statements on that system as now carried out. There are two series of towers, viz., one for producing acid on the principles of the Glover tower, and another for absorbing the nitrogen oxides, both series counting the same number of towers, *e.g.* three acid-producers, I., II., III., and three absorbers IV., V., VI. for making 18 tons of acid 60° Bé. The acid-producing towers must be protected in the climate of Central Europe by being cased in, but the absorbing-towers do not require this. The former as well require no special building, but only a protecting-casing against wind and snow pressure, carried by the towers themselves. Arrangements are made for dividing the gases in the usual way. The inside lining corresponds to that which is usual for Glover and Gay-Lussac towers. The acid is introduced in the tower ceilings by emulsionating apparatus without any highly-placed tanks, and the water in the form of sprays in the top of towers I., II., III., and IV. The acid running out of the producers I., II., and III. is pumped on to the absorbers IV., V., and VI., and *vice versâ*, so that the towers I. and VI., II. and V., and III. and IV. are in communication. The pipes conveying the acid to the Gay-Lussac emulsioners are cooled by water. The acid ultimately all passes through tower V. and there gets up to 60° Bé., so that the whole of the acid produced comes out with that strength. The tower space for retaining the nitrogen oxides is ample, so that the end gases from tower VI., after passing through a coke box for retaining any acid fog, show only 0·5 g. SO_2 per cubic metre on an average. The propulsion of the gases takes place by means of an exhauster placed at the end of the apparatus. For producing 18 tons acid 60° Bé. per diem a ground space of 40 × 8 = 320 superf. m. is required for the towers; the total cost in Germany is from £5000 to £5500; the cubic contents, counting only the lead space, about 600 cb.m. Hence, 1 cb.m. produced 30 kg. acid of 60° Bé. (equal to 37 kg. chamber acid of 53° Bé.) in twenty-four hours. Of this tower I. produces about 20 per cent., tower II. 30 per cent., tower III. 50 per cent., and the SO_2 is now oxidised down to mere traces. That means a duty of nearly ten times as much as that of ordinary chamber space, at a cost for plant of about half of that of the chambers for the same duty. The consumption of nitric acid of 36° Bé. averages 0·75 parts to 100 parts chamber acid. The power for driving the exhauster is 3 kw. per hour. The consumption of air for emulsionating is about 4000 cb.m. air, compressed to 2½ atm., and that of cooling-water from 200 to 400 tons per day. Hartmann enumerates the advantages of the tower system as follows:—1. Less cost of plant. 2. Less ground space. 3. Easy supervision of the plant. 4. Easy superintendence of the working. 5. Production of all the acid at a strength of 60° Bé. 6. Altogether less producing expense than that of the lead-chamber process. The first experimental plant was erected in Hruschau in 1908, a larger plant in 1909, a third in 1910, and a fourth in 1911. Ten or twelve plants were in course of construction at other places in Austria and other countries, most of which would be at work shortly.

Hasenclever at the end of 1911 (*vide suprà*, p. 688) reserves his judgment upon this (as well as on the Griesheim) plan; it remains to be seen whether the saving effected by smaller capital charges will not be counterbalanced by increased working expenses and repairs. The working requires, as he points out, careful supervision, as the consumption of nitre easily becomes heavy. In addition, the acid, through being continuously in contact with the packing material of the towers, will probably become more and more impure, even if the burner-gases are subjected to a preliminary purification.

Th. Meyer (*Z. angew. Chem.*, 1912, p. 203) makes use of Hartmann's communications on the Opl process for comparing the expenses of plant and working that process with those of the lead chambers. For a plant producing 18 tons acid of 60° Bé. per twenty-four hours = 6480 tons per annum, he comes to the sum of £2100 for the chambers and £800 for the Opl system, as cost of land and buildings, which means an advantage of £1300 in favour of the latter. The cost of chamber plant comes to £2250, that of the Opl towers to £1580, or an advantage of £670 in favour of the latter. (In both cases the Gay-Lussac and Glover towers are left out of the calculation, as these must be provided in either case.) Concerning the working expenses, the cost of producing the sulphur dioxide gases, that of the nitre and the water (steam) may be left out of the calculation, as being substantially the same in both cases. But the Opl process entails additional expenses for lifting the acid to the top of the towers, for the exhauster which drives the gases through the towers, and for cooling-water. Meyer gives his data for calculating that part of the working expenses for 100 kg. acid 50° Bé. at 22·1 Pfennig for the Opl towers, against 11·4 Pfennig for chambers, leaving a difference of 10·7 Pfennig per 100 kg. acid 50° Bé. *against* the Opl process, equal to 13·4 Pfennig for acid of 60° Bé., or, say, 1s. 4d. per ton of acid of 60° Bé. To this must be added the patent royalty which comes to about 2 Pfennig per 100 kg., or about 2¼d. per ton. The advantage claimed for the Opl process, that all the acid is obtained at a strength of 60° Bé. = 168° Tw., cannot be taken into account, as this result can be obtained with the chamber system as well; and it is loaded with the drawback that in the Opl process all the acid comes out in an impure state, like that of Glover-tower acid. The question of wear and tear cannot be settled up to the present, but this item is likely to be somewhat higher in the Opl system than in the lead-chamber system. One circumstance is undoubtedly in favour of the Opl system, viz., that it requires less ground space than the chamber system; and where the purity of the acid is of no consequence, there is a certain advantage of the Opl system in the smaller working expenses, as above stated.

E. W. Kauffmann (Ger. P. 226219) passes the burner-gases first through a dust-chamber with horizontal flues, and then, by means of a fan, into an iron tower, lined with brickwork, where the necessary water and nitrous gases are introduced and which is kept at 150° to 200°. The supply of water is regulated so as to produce acid of at least 60° to 62° Bé. (78 to 82 per cent. H_2SO_4), but it may go up to 98 per cent. [?]. The gases coming out of the tower pass through a cooler and into a Gay-Lussac tower; the nitrous vitriol here produced is denitrated in apparatus similar to the old "steam-columns" (*vide infrà*), from which the nitrous gases re-enter the reaction-tower. This process demands much less ground space, and the plant cools much less than ordinary chambers, and furnishes acid of much higher concentration.

Fels (Ger. P. 228696) employs, behind the Glover, a series of horizontal cylinders with central shafts and agitating-blades, which cause a thorough mixture of the gases with each other and with the bottom acid. The gases are driven through them by means of a fan, placed behind the Glover; they enter the cylinders in the centre and leave them at the top; the acid formed therein runs through them all in the opposite direction, any excess of it being removed by U-shaped overflows. This method makes it possible to work with an excess of nitrous gases.

Wentzki (Ger. P. 230534) employs several horizontal revolving cylinders in series. The gases are passed in and out through hollow axes, which project only a short way into the cylinders and are bent upwards there, as shown in Fig. 217.

On the inside walls of the cylinder longitudinal, bent shovels are placed, which during the revolution raise up the liquid, keep it permanently agitated and throw it against the walls. In the beginning the first cylinder is charged with nitrous vitriol or with a mixture of sulphuric and nitric acid; the other cylinders receive sulphuric acid. The burner-gases, propelled by a fan, enter into the first cylinder, where they are partly converted into sulphuric acid; the nitrous gases, here evolved, travel along with the remaining gases and are retained in the second and third cylinder. Gradually the acid in the first cylinder is denitrated and the contents of the second are changed into nitrous vitriol, and so forth. The same inventor (Ger. P. 238960) describes the same process, carried out in a series of cylinders, filled with a horizontal revolving stirring-apparatus, in *Z. angew. Chem.*, 1911, p. 2440. He describes his process, which is still in the experimental stage.

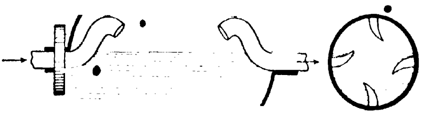


FIG. 217.

Petersen (*Chem. Zeit.*, 1911, p. 493; *J. Soc. Chem. Ind.*, 1911, p. 681) proposes, in lieu of towers, to pass the burner-gases through a series of shallow lead boxes, connected by pipes, and rising behind one another by steps of 30 cb.m. They are provided with perforated false bottoms, and packed above this with quartz. The first two boxes contain nitrous vitriol, the others sulphuric acid of sp. gr. 1·6 to 1·7. A fan draws the gases, cooled to 50° in a special cooler, through the acid in these boxes. In the first of these the SO_2 is at once transformed into H_2SO_4; the second prevents any escape of SO_2, and the evolved NO is absorbed in the third and fourth box. Acid of sp. gr. 1·6 is most suitable, as it readily absorbs nitrogen oxides, and is equally easily denitrated. Water is added in the gas cooler or in the first box to maintain the sp. gr. at 1·6. The inventor proposes also another system consisting only of two boxes, completely filled with quartz, and provided with short lead baffles, projecting down from the lid. The acid, as it flows through, fills these boxes completely, and the gases pass horizontally through, so that less pressure is required than in the first system. His third system has only a single box, and is otherwise like the second system.

His patents are: B. Ps. 15406 of 1907, 21346 of 1907, 27738 of 1907; Amer. Ps. 899898, 899899, 904147; Fr. Ps. 378454, 382262; Ger. P. appl. of 28th December 1905.

Chamber-fittings.

Every set of chambers must contain a number of auxiliary apparatus, which in part are absolutely necessary for the process, and in part serve to check it chemically and technically: the former are essentially those for introducing the nitre, the steam, and the air; the latter, smaller apparatus, will be described first.

Drawing-off the acid is never done by cocks attached to the chambers. Such taps might be made of hard lead (4 to 5 Pb to 1 Sb), but they would soon get stopped up with sulphate of lead, and could not very easily be repaired when leaking. It is best to place beside the chamber a round or square lead box, open at the top, of the same height as the upstand of the chamber-bottom, and connected at or near the bottom by a wide pipe with the chamber; or a suitable piece may be burnt on to the chamber, as shown in Fig. 218, and the connection made by a slit. The box may be provided with a stopcock; but more usually, as shown in the figure, it carries in its bottom a valve-seat, *a*, of

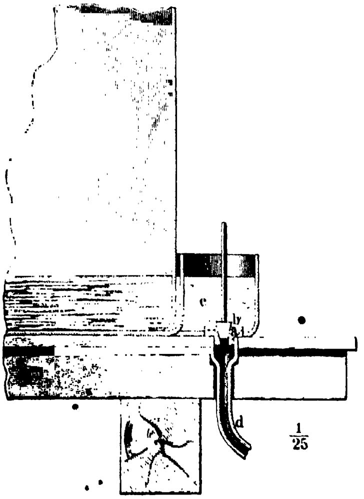


FIG. 218.

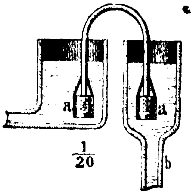


FIG. 219.

regulus metal, into which fits a conical plug, *b*, of the same metal provided with an iron handle covered with lead. The running-off pipe *d* is either burnt to the valve-seat or joined to it by an open funnel; the latter permits the running off to be more easily observed, but is apt to occasion running over, by getting stopped up. Or, as shown in Fig. 219, a lead *siphon* may be employed, with cups attached at each end, *a a*, which keep it always filled, so that it begins to act as soon as one of its limbs has been put into the acid. The second limb then enters into a large funnel of the running-off pipe *b*.

The simplest plan, which does not work at all badly, is this: to burn a short piece of thick lead pipe to the chamber-side, and make the joint very strong by casting lead round it. This pipe ends over the funnel of the running-off pipe, and is closed by a good india-rubber cork. The men take this out and put it in by hand, having a bucket of water standing by to wash the acid off their hands.

Another arrangement, shown in Fig. 220, is very good indeed. The siphon *b* is firmly attached to the box *c*, or within the

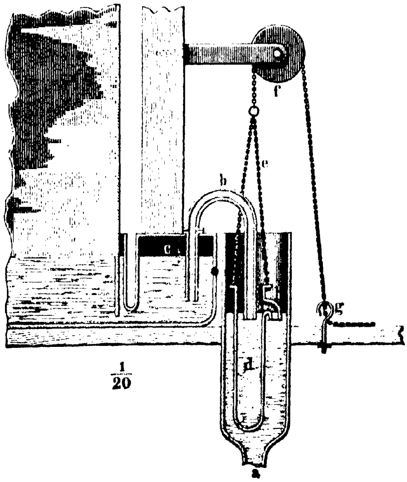


FIG. 220.

upstand of the chamber. A cylinder, *d*, surrounding the outer limb of the siphon, is so suspended that it can be drawn up or down by means of the chain *e* and the pulley *f*, and fixed in any position by the hook *g*. The cylinder *d* forms a continuation of the outer limb of *b*; when it is quite drawn up, so that its overflow *h* is at a higher level than the acid in *c*, it will cease to run; but when *h* gets below this level, the siphon will at once begin to act, all the more quickly the more *d* is lowered. Thus the acid can be run off with more or less speed and with the utmost cleanliness.

Fig. 221 represents a siphon suitable for hot acids in any part of the works. To the top of the siphon, *a a*, there is joined by a bent tube a closed lead vessel *b*, which by an elastic tube

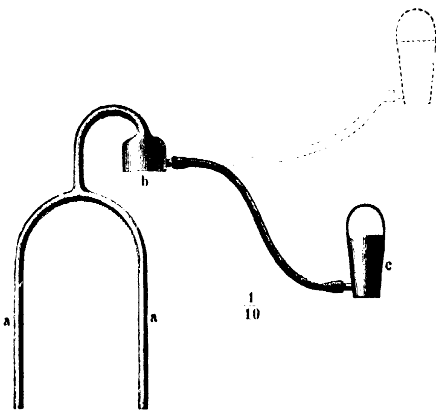


FIG. 221.

is connected with the open vessel *c*. The latter is filled with acid and lifted into the dotted position, whereupon *b* and then the siphon *a* are filled; *c* is then lowered, upon which the siphon begins to act, some acid running back from *b* to *c* and thus producing a partial vacuum.

We shall in this place also mention the best arrangements for *inserting siphons into glass carboys* or other vessels for carrying corrosive liquids. The simplest and most efficient plan is that shown in Fig. 222. A glass or lead siphon, *a*, is inserted into a good india-rubber cork, made strongly conical so as to fit bottles with various sized necks; another short tube, *b*, passes through the same cork. The siphon *a* may or may not be provided with a tap, *c*. It will be seen without further explanation that the siphon can be started by blowing into *b*. The flow of liquid may be stopped either by closing the tap *c*, or, if there is no tap, by lifting out the cork, or by opening a third hole provided in the cork for this purpose. In the (very frequent) case that the mouth of the carboy is too irregular in shape for the cork to fit air-tight, the remaining air-channels are stopped up with damp clay; and in an emergency a lump of damp clay may replace the india-rubber cork entirely.

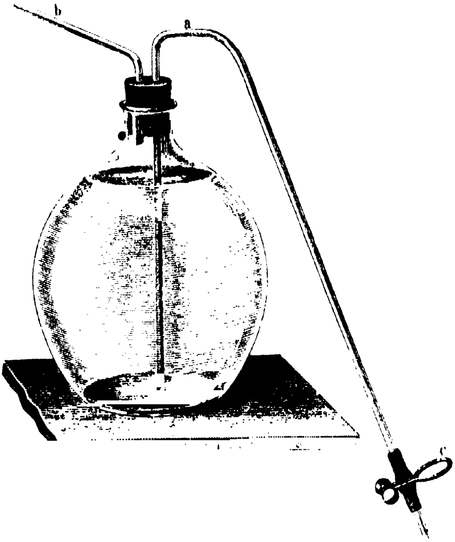


FIG. 222.

Bode and Wimpf's siphon (Ger. P. 23794; *Chem. Zeit.*, 1885, p. 907; *J. Soc. Chem. Ind.*, 1885, p. 484; further improvements in *Z. angew. Chem.*, 1889, p. 522) rests on a very similar principle, with addition of a ball-valve for stopping and starting the siphon. It seems to be specially adapted for nitric acid.

Alisch (Ger. P. 9133), Landel (Ger. P. 9307), J. P. y More (Ger. P. 28721), Opländer (Ger. P. 30662), and others have constructed different kinds of siphons.

De Hemptinne has written a pamphlet in which he traces a great many forms of siphons to their authors; but there is nothing specially new in it.

Pratt's carboy-emptier, sold by J. J. Griffin & Sons, London, is shown in Fig. 223.

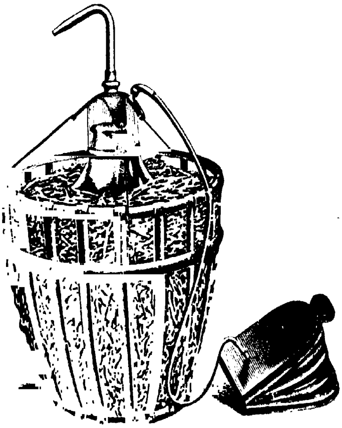


FIG. 223.

J. Cortin, of Newcastle-upon-Tyne, makes *non-rotative acid valves* of a special mixture of regulus metal, the plug rising or falling into its seat out of a fixed setting without turning round, so that it is free from friction in working, and the wear and tear are reduced to a minimum.

Acid-dishes (*drips, tell-tales*) are placed inside the chambers, in order to examine the process by ascertaining the quantity, strength, and nitrosity of the condensing acid. They are made in very different ways—for instance, that shown in Fig. 224. A is a lead vessel, burnt inside against the chamber-side about 3 ft. above the bottom. The acid caught here runs by the tube *a* through the chamber-side into the lead cylinder B, containing a hydrometer. B is provided near its bottom with a side-branch, *b*, rising above its top, and ending in a funnel for receiving the acid, which thus constantly runs in at the bottom and out at the top of B into a vessel, C, from which it is carried back by a small pipe into the chamber. The greater the length of A, the more quickly the acid will be renewed in B, and the more reliable are the indications.

Many manufacturers place S-shaped drip-tubes in the connection between the chambers for a similar purpose. Others do not trust to the collectors burnt to the chamber-sides, but place leaden or stoneware dishes at some distance from the side within the chamber. These rest on feet made of lead tubes, or upon a stand of stoneware, so as to be elevated above the level of the acid; and they have an outlet leading outside the chamber. In some works, both kinds of drips are fixed side by side; and it is noticed that those fixed to the sides always yield acid of 6° to 10° Tw. less than the inner drips, evidently because more aqueous vapour is condensed on the sides together with the sulphuric acid.

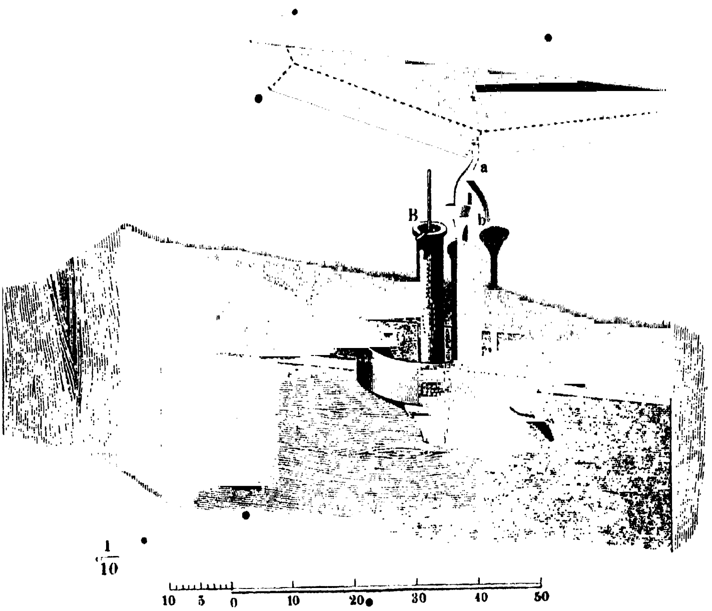


FIG. 224.

Firman and Cocksedge (B.P. 52 of 1909) describe drip-pans, with grooves, terminating in an acid-luted outlet, so constructed that no acid remains in the pan, which therefore shows the exact quantity of acid made in the chamber at the time.

Generally the cylinders of acid-drips are made far too large, so that they show the changes in the process much too slowly. It is therefore preferable in all respects to make the cylinders very small, say holding about 20 c.c, with a side tube and funnel, into which the fresh drips fall, as shown in Fig. 224, whilst the cylinder itself keeps overflowing, and thus its contents are renewed about once in every ten minutes. Special small hydrometers, having only a range of, say, about 20° Tw., are made for the purpose of showing the strength of acid in these small drips.

For taking samples of the bottom acid itself a recess is usually made in some part of the chamber by dressing back the lower part of the side. Some, in order to be quite sure, always take the sample out of the chamber itself through a special small manhole luted with moist clay; in this case there is a slight loss of gas, but no danger of getting stagnant acid. Such a manhole is shown in Fig. 225*a* in section. The large *manholes* may be made in exactly the same way; or else their lids may fit into a groove luted with damp clay, as shown in Fig. 225*b*. Large chambers are fitted with several acid-drips, manholes, etc.

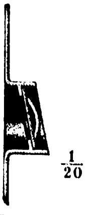


FIG. 225*a*.

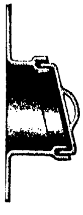


FIG. 225*b*.

For taking the samples themselves a dipper of lead or glass is employed, which is lowered slowly, so as to get a sample of all layers of the acid into it. There is often a great difference between the top and bottom acid.

Mostly *thermometers* are fixed at regular intervals of 30 to 50 ft. in the length of a chamber, whose mercury-vessel is inside, and whose scale is outside the chamber. This means of observing the temperature is undoubtedly infinitely better than the rough one formerly in general use in England, by touching with the hand.

For chambers not exceeding 100 ft. in length, one set of drips, thermometers, etc., is generally thought sufficient. For longer chambers this is not the case; at the German works there is generally a special set of these fittings for about every 60 ft. length of chamber.

The *pressure* inside the chambers might be indicated by any of the anemometers to be described at the close of this chapter, especially those of Vogt or Sorel; but usually simpler means are employed, such as ordinary glass pressure-gauges.

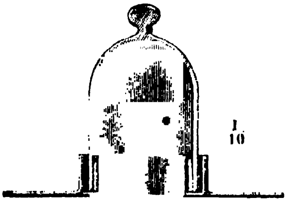


FIG. 226.

Sometimes stoneware plugs are put into holes made in the chamber-sides, in order to indicate the pressure inside the chamber. The tension of the gas is also seen by lifting the lids of the small manholes (Fig. 226), which are always placed on the top of the chambers with hydraulic lutes, and which generally consist of glass jars, so as to give light for observation through the side-windows (see below).

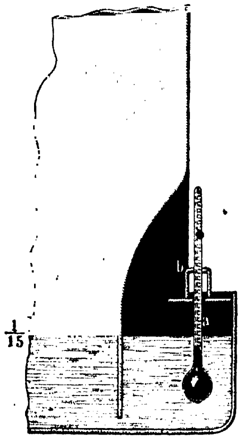


FIG. 227.

For *gauging the height of the acid* in the chambers we employ either stationary lead gauges (which, however, are difficult to read exactly), or accurately divided copper rods, which are dipped in every time, but always in the same place, since the chambers are never absolutely level, or glass floats like that shown in Fig. 227, the stem, *a*, of which slides in a small lead frame, *b*, whose upper edge serves as an index for reading-off. The float will sink more or less in the acid according to any alterations in its specific gravity. To make this cause of inaccuracy less sensible, the ball of the float is made pretty large. These floats are most convenient for reading-off.

An instrument for *mechanically calculating the weight of sulphuric acid in the chambers* is described by C. Davidson in *Chem. News*, lxxxvii. p. 205, and *J. Soc. Chem. Ind.*, 1903, p. 625.

A very great assistance in judging of the chamber-process is afforded by *glass windows* or *sights*, which permit the colour inside the chambers to be seen. Whoever has once got used to these windows will never do without them. They are 8 or 9 in. square, and are arranged at a convenient height for looking through, in those places in the chamber-side which lie in a line with the glass manhole lids in the chamber-tops; thus they are sufficiently lighted. Where the chambers are roofed in, light must be procured in some other way (for instance, by two opposite windows corresponding with a window in the chamber-shed, etc.). The chamber-glasses are put into small lead rabbets, and luted with white lead and boiled oil. The assertion is occasionally made that the colour of the gaseous mixture, observed across the width of the chamber, or in the diagonal line from the side to the manhole lid in the top, is too deep, and that "sights" in the connecting-tubes are preferable; but just the opposite is the case, since the observations are evidently far more accurate, and any alterations of colour much more easily perceived in the former than in the latter case. Only in the first part is the gaseous mixture, through copious condensation of acid, too opaque for observing its colour; but just there it is quite unnecessary, for only in the back parts of the set is it important to have always an excess of red vapours.

At some works they prefer to the ordinary side-windows, which are rather difficult to keep clean, glass jars, similar to those shown in Fig. 226, p. 701, but placed on special short wide branch-tubes, burnt in the sides of the chambers at convenient places. These jars when dirty can be exchanged in a moment for clean ones, and they are supposed to show all the changes in the chamber-atmosphere quite as well as the glass panes fixed in the lead walls themselves; but my experience is decidedly to the contrary, as sometimes the side-jars are quite yellow while the chambers are already pale, and *vice versâ.*

Apparatus for introducing Nitric Acid into the Chambers.

These are divided into two classes. In the first class the nitric acid enters the chambers in a state of *vapour*, mixed with the burner-gas, whose heat evolves it from a mixture of sodium nitrate and sulphuric acid contained in an iron pot. This is styled "potting." In the second class the nitric acid is made in a *liquid* form in special apparatus, and introduced as such into the chambers. Opinions still differ as to which of the two plans is best. The plan of introducing acid in the state of vapour, which was formerly general in England, but only rarely used on the Continent, has the advantage of greater simplicity and of saving labour and fuel. The advantage sometimes claimed for it, that there is less loss than by making and employing liquid nitric acid, is hardly a real one; for in the first plan some nitric acid is easily condensed during the conveyance of the gas to the chambers, and may corrode brick-work, iron, etc., whilst liquid nitric acid is always introduced exactly in the place where it is needed. It is necessary to employ much more sulphuric acid for the decomposition of the nitrate of soda in "potting" than in the regular manufacture of nitric acid. The presence of nitric acid in the burner-gas will also induce a premature formation of sulphuric acid, especially if it be much cooled; but the Glover tower obviates any inconvenience arising from this. On the other hand, some are afraid that in "potting" the nitre-ovens may get so hot that a portion of the nitric acid will be decomposed down to nitrogen protoxide or even to free nitrogen; but the men generally employ so much sulphuric acid for decomposing the nitre, that this cannot easily happen, nor are N_2O and N formed so very readily as was formerly supposed (see later on).

The advantages of introducing nitric acid in the *liquid* form are the following:—avoiding the entrance of false air into the chambers and the escape of burner-gas into the atmosphere, both of which occur in many (not all) systems of employment of gaseous acid; the possibility of employing as much nitric acid and as quickly as desired, whilst in the other case this depends on the heat of the burner-gas, which during a bad process, just when most nitric acid is needed, sometimes proves insufficient; lastly, and most of all, the exact regulation possible with liquid nitric acid and its continuous supply, whilst gaseous acid is always given off very unequally from the nitre-mixture.• These advantages have induced most continental and later on many English and American manufacturers to employ liquid nitric acid. Muspratt (*Dictionary of Chemistry*, ii. p. 1029) certainly reports that a continental manufacturer, who previously worked with liquid nitric acid, after having seen the use of solid nitre in England, had saved one-third of his nitre by introducing the English plan. This statement simply proves that that manufacturer had not been very careful before, and is no guide whatever. The opposite experience has been much more frequent. Liquid nitric acid, however, will do harm if the apparatus for introducing it is not constructed in such a way as to completely volatilise it or convert it into gaseous products before it reaches the chamber-bottom, since it will act upon this. Accordingly, sulphur dioxide and aqueous vapour, which decompose the nitric acid, must be brought into contact with it as completely as possible.

It is claimed as an advantage for introducing the nitre by "potting," that the chambers are not exposed to the damage possible in the case of incautious handling of nitric acid, whilst, on the other hand, the irregular evolution of gas from the nitre-mixture is equalised by employing several decomposing apparatus, and charging them in turns, say once every hour, just after a fresh pyrites-burner has been charged; thus the stronger evolution of nitre-gas runs parallel with that of sulphur dioxide. Some prefer a contrivance for supplying gradually, and not all at once, the sulphuric acid serving for decomposing the nitre. It was formerly contended that the best English works, all of which employed at that time solid nitre, worked with as small a consumption of it and as good a yield of vitriol as the best of the continental works employing liquid nitric acid; also on the Continent some manufacturers work quite as well with solid nitre as their neighbours with nitric acid; but it is extremely difficult to check such statements, as few manufacturers divulge their *real* working results to outsiders, and, moreover, very many of them do not even know these results themselves with that degree of accuracy which is required to decide this question.

There is no doubt whatever that the chamber-process can be worked more regularly by the continuous supply of nitric acid in the liquid form (*cf.* Eschellmann's experiments at Widnes, *infrà*); and the just objection to this, formerly existing, that there was a risk of damaging the first chamber in case of a collapse of the "cascades" (see p. 712) has been entirely removed, in the first place by the almost general plan of introducing the nitric acid into the Glover tower, and in the second instance by spray-producers, etc. The labour of making nitric acid in large apparatus and condensing it in receivers is not much greater than that of frequent "potting"; the waste of sulphuric acid for decomposing the nitrate of soda is much less in the former than in the latter case. The nitric-acid retorts are even sometimes heated by pyrites-burner gases. These reasons explain why the majority of continental manufacturers always preferred the employment of liquid nitric acid for the chamber-process, and later on probably most of the English and American manufacturers have gone over to it as well.

Introduction of Nitric Acid as Vapour ("Potting").

The apparatus serving for this has been partially described in a former chapter (pp. 393, 394, 396, 402, 440), when treating of the sulphur- and pyrites-burners. The drawbacks have been pointed out which attend placing the nitre-pots within the burners, or, generally, in such a way that the acid sulphate boiling over can run into the burners. Later on, however, there was always a special *nitre-oven* constructed by enlarging a suitable place in the gas-flue. It is situated either above or, preferably, just behind the burners, and provided with the necessary working-doors and a cast-iron saucer for collecting what boils over. The nitre-pots themselves have various shapes —for instance, that shown in Fig. 228; at *a′ a* ledges are cast on the bottom, which facilitate pushing the pots backwards and forwards. They hold from 8 to 12 lb. of nitre.

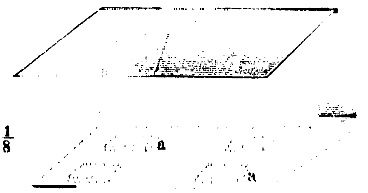


FIG. 228.

The "potting" with these pots, which are still (or have been until recently) met with in some English works otherwise abreast of the times, is very troublesome and imperfect.

A much more perfect plan is that of decomposing the nitre in a *fixed apparatus*, and running off the acid sodium sulphate (nitre-cake) in a liquid form. This apparatus consists of a semicylinder of cast iron, *a* (Figs. 229 and 230), with a cast-on tube, *b*, bored somewhat conically. The latter projects out of the nitre-oven, and during the working is closed by a ground-in iron plug with a long handle. Outside there is a cast-iron saucer for holding the nitre-cake, which at once solidifies. The internal saucer, *c*, catches any stuff boiling over. The nitre is introduced by the hopper *d*, which is provided with a damper; and after putting in the damper again, it is made gas-tight by filling up with the next charge of nitre. An S-shaped tube (not shown in the diagram) serves for running in the sulphuric acid, for which it is best to provide a small tank with a siphon or stopcock. The acid should be run out of this tank by a pipe with a very fine point into the S-shaped tube, so that the running shall take a long time, and the nitre be only gradually decomposed. Sometimes an iron scraper with a long handle (passing through one of the ends of the oven) serves for stirring up the mixture in the pan. The hole for this must be kept air-tight with clay. An apparatus of the size drawn here holds 56 lb. of nitre, which can be easily decomposed in two hours. In any case there should be two or more of these apparatus, so

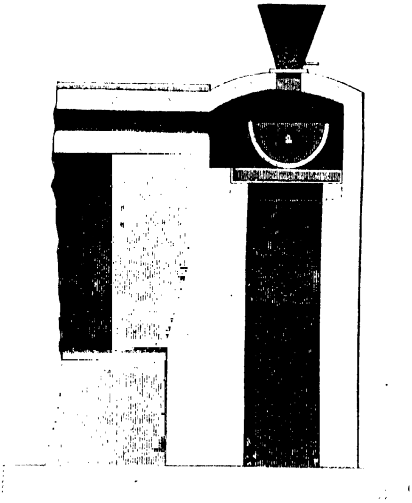


FIG. 229.

as to make the current of nitre-gas more regular by charging them in turns.

Even preferable to the arrangement here shown is that of placing the nitre-trough in such a way that the burner-gas can play round the bottom as well. The saucer for the boiling-over stuff, which forms the bottom of the nitre-oven, must then be placed somewhat lower.

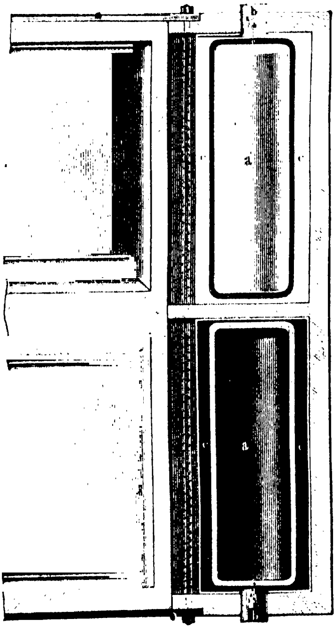


FIG. 230.

At Oker the potting is effected in cast-iron retorts set in the high kilns used there (p. 421); the gas-delivery pipe opens into the gas-flue belonging to the kilns.

Rice (B. P. 16757 of 1892) patented a contrivance which had been in operation in several places for many years past, viz., putting the nitre-oven between the burners and the Glover tower in such a way that, by means of valves, the burner-gas can be made to travel either through the oven or directly into the chambers.

A. P. O'Brien (Amer. P. 694024) describes a cylindrical oven, through which the pyrites-gases are driven by a fan, with many details of construction.

An intermediate process between the "potting" system and the application of liquid nitric acid is the generation of nitric acid in the ordinary retorts, fired with coals (pp. 139 *et seq.*), but without condensing the vapours to liquid nitric acid by passing them straight into the chambers. This system, which was followed in several English works about 1880 (Jurisch, *Schwefelsäurefabrikation*, p. 130), seems to have neither the simplicity and (apparent) cheapness of potting in the nitre-oven, nor the exact regularity of supply by liquid nitric acid. It costs as much coal and very nearly as much labour as the latter; and the passage of the vapours from the nitric-acid retorts to the chambers presents great difficulties on account of the unavoidable condensation of liquid acid, which is not entirely overcome or rendered harmless by lining the cast-iron pipes with stoneware pipes, with an asphalt or asbestos cement between them. If an acid-maker once emancipates himself (as he ought!) from the old system of "potting," he should proceed to the thorough reform of making and using liquid nitric acid.

The Soc. anon L. Vogel (B. P. 6846 of 1904; Ger. P. 171088) passes the vapours evolved in the ordinary nitric acid retorts from sodium nitrate and sulphuric acid without condensing them to liquid acid, into the Gay-Lussac tower, where they are absorbed and later on utilised in the Glover towers. Thus large quantities of nitric acid can be supplied to the chambers in a continuous manner, assisted by a fan interposed. The cylinders, where the nitric acid is evolved, are set in the dust chamber behind the kilns and heated by the burner-gases.

Pozzati (Fr. P. 404708) passes the nitrous gases from the nitre-ovens directly into the chambers, instead of taking them through the Glover tower [a proceeding quite generally taken many years previously, but abandoned for better methods later on].

Dervig (Amer. P. 850820) in lieu of the ordinary nitre-ovens employs a column, packed with quartz or coke, through which a solution of sodium nitrate in sulphuric acid is run; it is either placed between the pyrites-burners and the Glover tower, or between this and the first lead-chamber. In the first case part of the hot burner-gases, in the second the whole of the Glover exit-gases are passed through this column (which has about one-fifth of the diameter of the Glover), in order to supply the necessary heat for driving off the nitric acid. [The reporter in *Chem. Zeit. Rep.*, 1907, p. 272, justly remarks that this column will be easily stopped up by sodium sulphate crystallising out.]

Introduction of Liquid Nitric Acid.

Any of the apparatus previously described (pp. 139 *et seq.*) for the manufacture of nitric acid may be employed for use in connection with acid-chambers, but no special precautions are in this case needed for obtaining the acid in a concentrated state or free from lower nitrogen oxides. On the contrary, any low-strength and impure acid obtained in the manufacture of commercial nitric acid may be turned to use in the vitriol-chambers.

It is, however, of the greatest importance for the process to supply the acid in an even, continuous way, and to regulate the supply to a nicety. This can be most simply done by a *Mariotte's vessel*, as shown in Fig. 231 on a scale of $\frac{1}{10}$. The stoneware vessel, A, containing the nitric acid, is closed by a caoutchouc cork, *a*, holding a glass tube, *b*. The latter is the only channel for the air, which must take the place of any acid running out through the cock *c*. As the liquid above the level *h h'*, down to which the tube *b* reaches, is supported by atmospheric pressure, only the height of acid below this can influence the speed of outflow; and this remains constant till the level of the acid has sunk below this point. The glass water-gauge, *d*, and the lead scale, *e*, admit of observing the height of liquid within the vessel. The latter is filled up through the tube *b*, which ends in a funnel at the top. During the filling either the cork must be raised, or it must be provided with a separate open glass tube which at other times is kept closed. The funnel *f* carries the acid into the glass or stoneware pipes conveying it into the chambers.

At some works there are two tanks which are filled up in turn, one of them every twelve hours, or both every twenty-four hours. The acid is continually running out of both tanks. When one of them is half empty, the other is just full; and thus

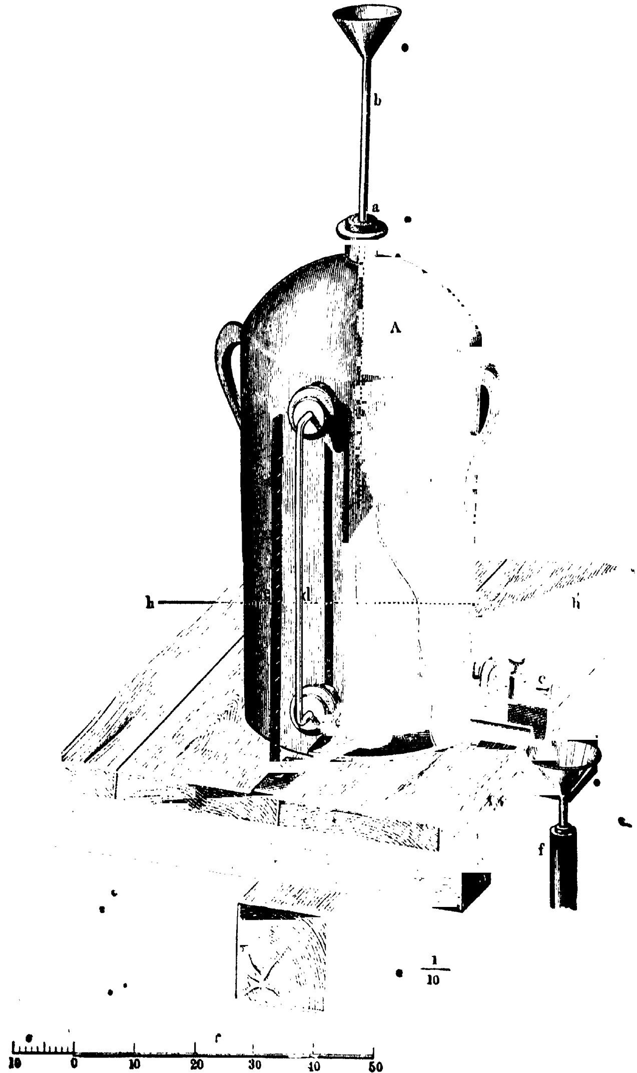


FIG. 231.

the variation of pressure is compensated to a certain extent; but this plan cannot at all vie in regularity with a Mariotte's bottle.

The Mariotte bottles sometimes become stopped up by grains of sand, etc., getting into the slightly opened stopcock. Bode (*Dingl. polyt. J.*, ccxx. p. 538) avoids this by opening the cock full bore, stopping the neck of the bottle tightly by a caoutchouc stopper (as shown in Fig. 232), through which a tube, *a*, goes down to the desired depth, and is connected by an elastic tube, *b*, with a metal or glass cock, *c*, of $\frac{1}{8}$ in. bore, which serves for regulating the supply. Further improvements in this apparatus have been made by M. Liebig (Post's *Z. f. d. chem. Grossgew.*, 1878, part 2).

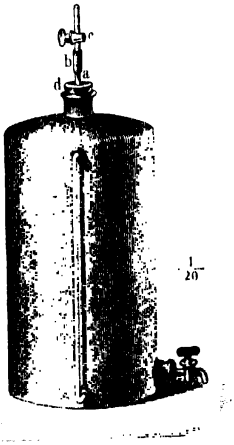


Fig. 232.

Formerly the nitric acid used to be introduced in one or two "*tambours*" (that is, small lead-chambers) about 22 × 10 × 12 ft., or cylinders of 10 to 13 ft. diameter and 12 ft. height, placed between the burners and the main chamber. The second of these contained the "cascades" or other spreading-apparatus; it stood at a higher level than the first tambour, into which it emptied its acids, and which only served for further exposing it to sulphur dioxide and completely driving off the nitrogen oxides. This first chamber received enough steam to prevent the formation of chamber-crystals, or to decompose them if they arrived in solution from the second chamber; the acid collecting in the first small chamber ran away into the main chamber. The first tambour is unnecessary; with proper regulation the nitric acid can be completely decomposed in the first apparatus by means of SO_2 and steam; but the latter ought to be supplied to such an extent that the sulphuric acid formed contains rather more than four molecules of water to each molecule of acid. At some French works the above-described faulty arrangement of the cascades caused the acid in the second tambour to contain a good deal of nitric acid.

The tambours have been mostly abolished, and the process is carried on in the main chamber; where the nitric acid, as is now usual, is introduced through the Glover tower, the tambours are entirely unnecessary.

Some manufacturers prefer not to run the acid continuously in a very small jet, but *intermittently* in larger quantities. For this a *siphon* arrangement is mostly employed (Fig. 233). *a* conveys nitric acid into the stoneware vessel *b*; through its bottom passes a tube reaching about three-fourths up its height, and open at both ends. This is covered by the wider tube *d*, which is closed at the top and open at the bottom, so that the acid fills up the space between the inner tube and *d*. As soon as it has got to the top of the former, this, together with *d*, forms a siphon which almost directly empties the contents of *d*, whereupon this is slowly filled till the acid has again risen to the top of the inner tube, and so forth.

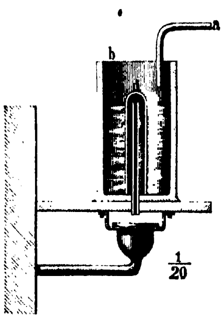


FIG. 233.

Cascades.—If the nitric acid were simply run into the chambers, it would cause very great mischief. It would dissolve in the chamber-acid and quickly destroy the chamber-bottom; moreover, much of it would find its way outside together with the chamber-acid without doing its duty within the chambers. It is therefore necessary that no nitric acid should arrive as such at the bottom of the chambers, but that, before reaching there, it should be decomposed into gaseous oxides of nitrogen. This is done by exposing it to the action of sulphur dioxide, that is by the chamber-gases themselves. Before the introduction of the Glover tower, and even long after, no other means were known for this purpose than spreading the nitric acid out over a large surface so that it was thoroughly exposed to the chamber-gases, and nothing could reach the bottom in an undecomposed state. This was done by means of stoneware or glass "*cascades*," of which there existed many descriptions, which are fully explained and illustrated in the first edition of this work, pp. 308 to 318.

Since these cascades have been almost entirely superseded by the Glover towers, we will here show only one of the best descriptions of cascades, that made by Fikentscher, of Zwickau, and shown in Fig. 234. The acid run into its top is spread over a large surface before reaching the bottom.

A fault inherent to all such systems is this: that there is no really practical way of knowing whether the nitric acid has been entirely decomposed before the chamber-bottom is reached. The means adopted for this end at some works leave much to be desired.

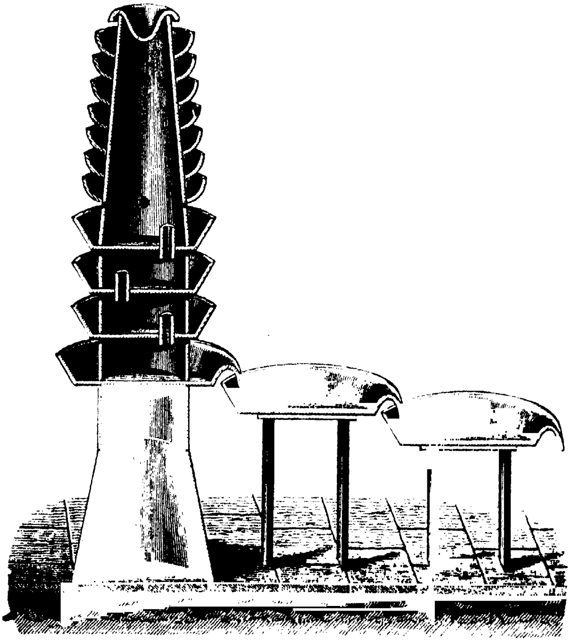


FIG. 234.

By far the simplest method of feeding, which dispenses with all cascades, tambours, etc., is that of *running the nitric acid together with the nitrous vitriol through the Glover tower.* Few manufacturers ventured to do this at first, because a loss of nitre was apprehended by following this plan; but at most of the best-managed works it has been done for many years past without involving any extra consumption of nitre, and it may be safely asserted that wherever a Glover tower in proper working order exists, no other apparatus is required for feeding the chambers with nitric acid. Hartmann and Benker (*Z. angew. Chem.*, 1906, p. 135) confirm this again.

This is a principle universally accepted, and borne out not merely by the practice of nearly all sulphuric-acid works where liquid nitric acid is used, and where a Glover tower forms part of the plant, but also by the practice of all the works following the formerly universal English plan of "potting" nitre between the burners and the Glover tower (p. 707). It is all the stranger that in a modern treatise on the manufacture of sulphuric acid (Jurisch, *Schwefelsäurefabrikation*, pp. 135 and 153) the old story is repeated of a great loss of nitre in the Glover tower by reduction to N_2O or elementary N, on the strength of some absolutely inconclusive experiments made by Vorster, and refuted twenty-five years ago by me (*cf.* Chapter VI.), and of some alleged "experiences" made in the North of France, without any proof by positive data. Wherever figures are given, *e.g.* Hurter's experiments of 1877, Jurisch is compelled to concede that with careful work no more nitre was used after introducing the Glover tower than before.

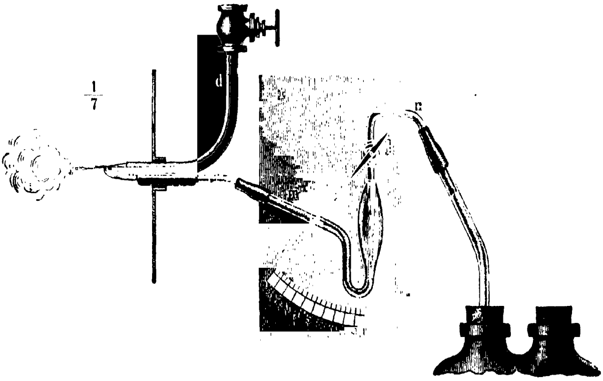


FIG. 235.

Sorel (*Fabrication de l'Acide sulfurique*, 1887, p. 204) states, as the positive result of the experience of the St Gobain works, that there is *no* destruction of nitric acid in the Glover tower.

Since in some cases a Glover tower is not available for the introduction of nitric acid, we shall describe a very efficient *spray-apparatus*, constructed for this purpose by Max Liebig (*Z. Verein. deutsch. Ingen.*, 1879, p. 111). It consists of a lead steam-pipe, *d* (Fig. 235), with a platinum nozzle, parallel to which runs a glass pipe, *m*, for conveying the nitric acid, bent up in front and drawn out into a fine point. The steam rushing past this causes a vacuum in the glass tube, and sucks acid through the latter from a stock-bottle, a glass cock, *h*, regulating the supply. The acid is spread out into a fine mist, and none of it arrives at the bottom undecomposed.

An apparatus for the same purpose, constructed by Mr Stroof, of the Griesheim works, has been made known to me by that gentleman, and is illustrated by Figs. 236 and 237.

Fig. 236 shows the general disposition, Fig. 237 the details of the injector *b*. The nitric acid runs from a Mariotte's bottle A into a Woulfe's bottle B, standing in a glass dish, provided with an overflow-pipe *c*, which conveys the acid, in case of the injector breaking down, on to the cascade C. From the bottle B the acid is sucked away by the glass injector *b*, whose steam-jet is connected with the steam-pipe *a* by a stuffing-box. Such injectors are best made of well-annealed water-gauge pipes drawn out to a point. The point projects but loosely into the suction-pipe, so that a little air is sucked in as well, and no breakage can take place by expansion. At a pressure of 1½ atm. the injector can carry away 16 cwt. of nitric acid in twenty-four hours in the form of spray, together with a little air. The mouth-piece of the injector must be contracted and widened out again, like that of a fire-engine, to prevent any larger drops forming at that place. The acid is thus completely converted into a mist, and a sensible saving effected in comparison with cascades.

Another glass injector for nitric acid has been described by Burgemeister (Fischer's *Jahresber.*, 1880, p. 228). He employs a platinum nozzle (*not* soldered with gold!) and a steam-jet placed just below, the latter consisting of a platinum nozzle, about ⅛ in. wide, inside the chamber, continued outside into a copper tube. Both tubes pass through a lead pipe burnt into the chamber-side, and are fastened in this with glycerine-lead cement.

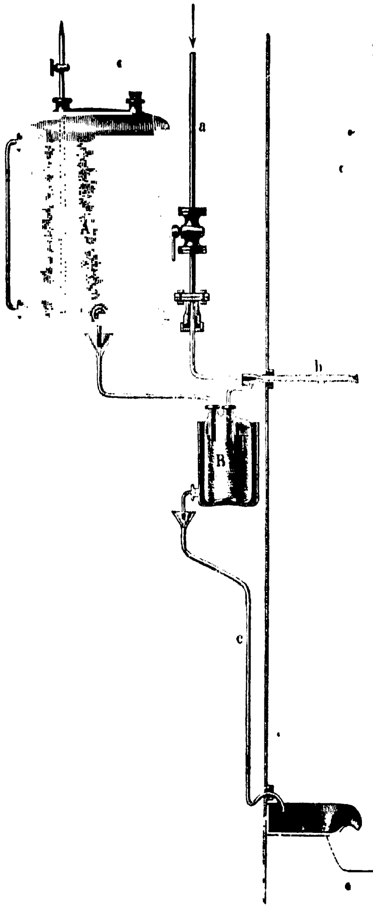


FIG. 236.

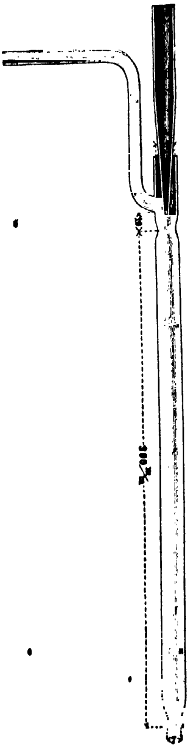
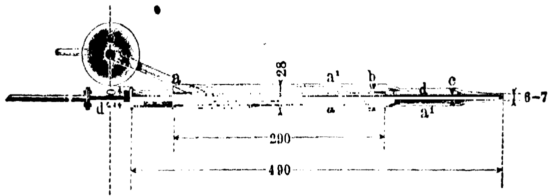


FIG. 237.

At the Freiberg works, where, in consequence of the complete cooling of the roasting-gases, they do not employ a Glover tower, formerly the nitric acid was introduced by cascades.

These have been replaced by glass injectors, constructed by Wolf, as shown in Figs. 238 and 239. A glass tube, a^1, 28 mm. wide, is sealed to a narrower central tube, a^2, at the place *a*. At *b* there are three glass knobs for steadying the inner tube a^2, and at *c* four small glass knobs for steadying the platinum capillary *d*. Tube a^1 is provided with a funnel *e* for running in the nitric acid. The tube *d*, made of platinum-iridium, is connected with a steam-pipe, and is held in the centre of pipe a^2 by an india-rubber cork *f* and the knobs *c*, *c*. The outlet of a^1 is 6 or 7 mm. wide. The nitric acid flows through *e* into the annular space between a^1 and a^2, and is sprayed into the chamber by the steam issuing through the platinum capillary. The whole is inserted into the chamber-side by means of an india-rubber joint at *g*, so that it is easily taken out and cleaned.

FIG. 238.



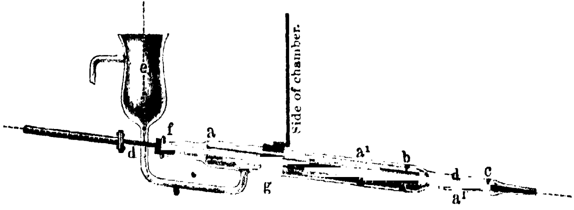


FIG. 239.

Potut (B. P. 7710 of 1900; Ger. P. 122920) introduces the nitric acid (or nitrate of soda solution, *cf.* later on) by a steam injector into the pipe leading from the Glover tower to the first chamber; he makes the ridiculous assertion that thus two-thirds of the nitre are saved in comparison with running the nitric acid down the Glover tower or straight into the first chamber.

Other manufacturers inject nitric acid into the last chamber (*cf.* next Chapter).

The simplest way of introducing the nitric acid through the Glover tower is to run a suitable quantity of it into the nitrous-vitriol tank at the bottom of the tower, and pump up the mixture in the usual manner. It is sometimes preferred to carry the nitric acid to the top of the chambers or the tower, and to run it into one of the lutes of the tower as required.

The Société Nitrogène (Fr. P. 404971) employs for the chambers a solution of dilute nitrous gases in concentrated sulphuric acid, thus producing a mixture of nitrosyl-sulphuric acid and nitric acid.

The storing of nitric acid on the top of the chambers or of the Glover tower is generally effected in large stoneware receivers, or else in a number of smaller stoneware jars or ordinary glass carboys, all of which are connected by glass siphons, so that the running off by means of a tap-siphon need take place only from the last vessel of the set (Fig. 240).

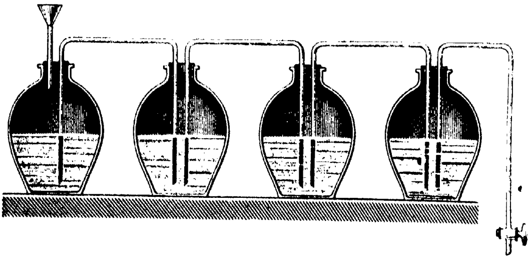


FIG. 240.

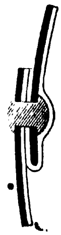


FIG. 241.

Vessels proof against nitric acid may also be composed of single pieces of stone joined together by a cement made of finely-ground asbestos and a dilute solution of silicate of soda, kneaded into a putty and preferably mixed with ground sulphate of baryta.

E. Pohl (Ger. P. 30188) employs iron vessels lined inside with asbestos cloth soaked in paraffin. The riveting of the iron shell is effected in the manner shown in Fig. 241, so that the acid nowhere comes into contact with the iron.

G. P. Adamson (Amer. P. 846541) stores acids in bottles of glass, ceresin or other suitable material, whose sides and bottoms are strengthened by a cylinder and plate of wire-gauze, embedded in the material of the bottle. The lower edge of the gauze cylinder has a head formed on it which projects below the edge of the gauze plate.

Introducing Nitre as an Aqueous Solution of Sodium Nitrate.

There is yet another way of introducing the nitre. Many years ago several works ran their nitre as a *solution in water* into the chambers. This has long since been discontinued, both because all the sodium sulphate formed gets into the acid, which is not allowable for many purposes, and because the lead always wears away very quickly at the point where the solution enters. The same method was patented by Burnard (14th August 1875). The solution of nitre was to be injected into the chamber in a thin jet, or, better still, at once mixed with sulphuric acid by means of a steam-jet, exactly similar to Sprengel's water-spray (*vide infrà*). The chief object sought to be attained in this process was an imaginary saving of nitric acid, which in the decomposition of nitre by the burner-gas was supposed to be reduced to N_2O and N. It has been mentioned on p. 337, and will again be referred to in Chapter VI., that no sensible decomposition of this kind takes place at all; and any advantage accruing therefrom would be far more than counterbalanced by the difficulty of keeping the nitrate solution long enough in suspension to completely decompose it and to prevent liquid nitric acid from getting at the chamber-bottom. The process also takes so much steam that the acid in the first chamber gets too weak. This is certainly contradicted by the patentees (*Chem. News*, xxxvii. p. 203); but no independent favourable testimony has yet been published, and a saving of nitre appears out of the question. It would, however, seem feasible to run a solution of nitre through the Glover tower together with chamber-acid and nitrous vitriol, so that the nitre would be decomposed in the tower itself, sodium sulphate and nitrous vapours being formed. Of course this plan, as well as that mentioned before, is restricted to the case of the sulphuric acid not being intended for sale, but employed for decomposing salt, or for the manufacture of superphosphates, etc.

The introduction of the nitre in the form of an aqueous solution of sodium nitrate is undoubtedly the simplest imaginable plan for supplying it to the chambers, uniting the advantages of both solid nitre and nitric acid—easy regulation, introduction of any quantity at a time, dispensing with all apparatus for introducing the nitre or manufacturing nitric acid, saving of labour and coals (in the case of nitric acid), avoiding the handling of nitric-acid carboys or of fluxed nitre-cake, the latter being an article difficult to utilise to any extent. Unfortunately these advantages are counterbalanced by a drawback, which has induced most manufacturers who have tried this process to give it up: it is found that sodium sulphate crystallises in the towers, tanks, and connecting-pipes and causes obstructions. It would be necessary to have two Glover towers for each set, and to run the nitre solution down only one of these, whose acid would not be used for the Gay-Lussac tower, but for the salt-cake pans or for superphosphate only. This would be very inconvenient, and for smaller works not at all feasible.

Blinkhorn (B. P. 1084 of 1878) runs a solution of sodium nitrate, of sp. gr. 1·35, in a regular jet upon sulphuric acid contained in a pot heated by the burner-gas, and draws off the solution of sodium sulphate from time to time. This will hardly decompose all the nitrate!

Potut (B. P. 7710 of 1900) injects a solution of sodium nitrate between the Glover tower and the first chamber (*cf.* p. 717).

Feeding the Chambers with Nitrous Gases obtained as By-products.

Several proposals of this kind, partly carried out in practice, have had no lasting success. Thus, for instance, the attempt has been made in France to obtain *oxalic acid* as a by-product in evolving the nitre-gas by heating molasses with nitric acid and conducting the vapours into the chambers. The yield of oxalic acid, however, was not large enough to compete with its manufacture from sawdust by fusing caustic potash. Not more successful was a proposal of Laing and Cossins, to heat sodium nitrate with arsenious acid or chromium oxide, in order to obtain *arseniates* or *chromates*, together with nitrous acid for the chamber-process (Wagner's *Jahresber.*, 1862, p. 207). It is also quite feasible to convey any nitrous gas generated in making arsenic, antimonic, phthalic acid, etc., by means of nitric acid, which formerly used to be lost, into the lead chambers; but this process, which (like all similar ones) can hardly be so conducted as to give a sufficiently *regular* supply of nitre to the chambers, is no longer called for, since the respective works now regularly regenerate nearly the whole of the nitric acid by mere contact of the vapours with an excess of air and water in "plate-towers" or similar apparatus (*cf.* pp. 183 and 659).

An ingenious process, invented by Dunlop, was for many years carried out by Messrs Tennant at St Rollox, and had become very famous, but it was not introduced at the new works at Hebburn erected by the same firm. A mixture of common salt, nitrate of soda, and sulphuric acid is heated in large iron cylinders; the principal reaction setting in is as follows:—

$$3SO_4H_2 + 2NaNO_3 + 4NaCl = 3Na_2SO_4 + N_2O_3 + 4Cl + 3H_2O;$$

but any further deoxidation of nitric acid must be prevented by keeping within certain limits of temperature. Thus there remains a soluble residue of sodium sulphate, whilst chlorine and nitrous acid are given off in a gaseous state. The two gases are separated by passing them through a series of leaden Woulfe's bottles filled with sulphuric acid of 1·75 sp. gr., which retains the nitre-gas, being converted into "nitrous vitriol" and used as such (*vide infrà*); the chlorine passes through without absorption and is utilised for bleaching-powder. The advantage of this process is, that chlorine is obtained direct from salt without making any hydrochloric acid and without employing peroxide of manganese. The drawbacks are:— that the nitre-gas has to be evolved again from the nitrous vitriol, which at that time could only be done by diluting with hot water, necessitating a reconcentration of the vitriol; that there is a danger of losing nitrogen compounds; and that the apparatus is very complicated. This process consequently did not obtain permanent success, and we abstain from giving a fuller description of it here.

At the Uetikon works, near Zurich, nearly all the nitre required for the chambers was for a long time obtained in the manufacture of *iron mordant* for dyeing purposes. This is made by treating ferrous sulphate with nitric acid, and thus oxidising the ferrous to ferric sulphate. The nitric acid is thereby reduced mostly to lower oxides of nitrogen; these gases are conveyed into the vitriol-chambers, and there do exactly the same duty as if the nitric acid had been directly supplied to the chambers. Recently the manufacture of *cupric sulphate* from metallic copper, sulphuric and nitric acid has been introduced at the same works, equally carrying all the nitrous vapours into the vitriol-chambers.

Supply of Water to the Chambers.

The water required to produce H_2SO_4 and to dilute this to the point required for the practical working of the chambers must be presented to the gases in as fine a state of division as possible. This was formerly in all cases and is still mostly effected by injecting into the chamber a certain quantity of *steam*, which rushes forward and on its way is condensed to a mist of very fine particles of liquid water. At many works, however, water is now injected in the shape of a mechanically produced spray.

The Steam

is always generated in an ordinary steam boiler, since boilers placed above the sulphur-burners have been given up everywhere. The boilers are constructed in the usual manner, but are mostly made for low pressure, rarely working above two atm., more frequently only at 1 or 1½ atm.; in the south of France they work at 3 or 3½ atm. A high pressure has no object so long as the liquid is spread over the whole chamber-space; for even low-pressure steam fulfils this requirement and sufficiently assists the draught. Low-pressure steam is more easily kept at a uniform tension than high-pressure: without this no regulation of the supply of steam to the chambers by the attendant is of any avail. High-pressure steam certainly condenses less readily than low-pressure steam; but this is a doubtful advantage, so long as the steam possesses enough "carrying-power" to convey the minute globules of water right to the other end of the chamber. Experience has shown that this is the case even with low-pressure steam; at many English works they employ only a single jet at one end of each chamber, and consider this quite sufficient to supply the whole chamber with moisture, but I do not like this practice (see p. 726).

Of course low-pressure steam may be obtained from a boiler working at high pressure by means of a reducing-valve. Thus at the Oker works the steam-pressure in the boilers is 3 to 3·5 atm., and is reduced to 1 to 1·5 atm. for feeding the chambers. At small works the same boiler may be utilised for supplying the chambers and for driving the machinery of stone-breakers, air-pumps, and so forth.

It is also almost a matter of course that the chambers may be fed with the exhaust-steam of engines, if these are worked in such a way as to leave some pressure in the exhaust. The utilisation of the waste steam of the Gay-Lussac air-pump for this purpose had been practised by myself for many years, as described in the first edition of this work (1879), Vol. I. pp. 393 and 565. A proposal not essentially differing from this was patented much later by Sprengel (B. P. 10798 of 1886).

The Societè L. Vogel, Milan (B. P. 17794 of 1904) procures part of the steam for the chambers by taking away part of the burner-gas before entering the Glover tower, and passing it through a tower packed with stoneware rings or the like, which is fed with water or dilute sulphuric acid, whereby steam is produced and then sent into the chambers.

At some large works, in order to control the uniform tension of the steam, so important for the regularity of the chamber process, *registering steam-gauges* are employed, which show the tension during the whole day on a sheet of paper wrapped round a drum making one revolution in twenty-four hours. Such a gauge, made by Schaeffer and Budenberg, of Magdeburg, is described in *Dingl. polyt. J.*, ccxvii. p. 519.

The *conveyance of the steam* to the chambers usually takes place in cast-iron pipes, with one or more branches for each chamber. The main-pipes in any case, and, if possible, also the branch-pipes, considering their great length, should be surrounded by bad conductors of heat in order to restrict radiation as much as possible, and to avoid a considerable loss by condensation of water.

The pipes must always be laid with a slight fall towards the boiler, so that the condensed water may run back. Where, from ocal circumstances, this cannot be done, automatic apparatus for removing the water should be fixed at the lowest points.

Of course the size of the main-pipes must correspond to the number and size of the chambers. When more than one steam-boiler is required, they are placed together and their main-pipes connected so as to equalise the pressure. The *branches* for each chamber need not be above 1 in. wide, even for large chambers (up to 70,000 cub. ft.) supplied by one jet. They are made of wrought-iron tubes, *a* (Fig. 242), sometimes of copper, up to a short distance from the chamber, where they end in a cock or valve, *b*, to which a lead pipe, *c*, equal in width to *a*, is attached and projects into the chamber itself. It is not, however, burnt to the chamber-side, *e*; but a short wider tube, *d*, is burnt to this, and *c* is loosely put into it, the joint being made tight with tar, cement, etc. Sometimes in lieu of this an india-rubber cork is employed, but this does not last long. In the latter case, if the outlet is stopped up by lead sulphate, the pipe c can easily be drawn out and cleaned and no platinum nozzles are required (as had been proposed by Scheurer-Kestner).

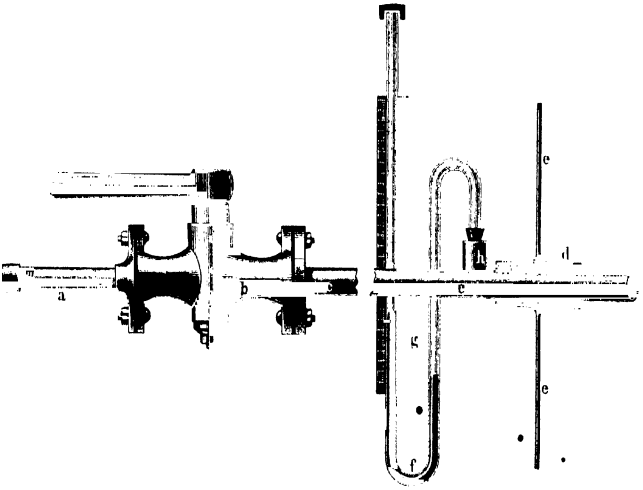


Fig. 242.

The same cut shows another commendable contrivance, viz., a simple mercurial *pressure-gauge*, consisting of a bent glass tube, *f*, with a scale, *g*, connected by means of a caoutchouc bung with a branch, *h*, of the lead pipe *c*. Thus the pressure *behind* the regulating-cock can be observed at any time; and the chamber-manager has thus a means of very accurately regulating the supply of steam. Any water condensed in the gauge can be easily allowed for.

A good *steam-cock* is preferable to a wheel-valve, because the wheel does not show how far the valve is opened whilst the handle of the cock can be fitted with a graduated arc so that its position can be fixed with precision.

Automatic steam-regulators, if reliable, save a great deal of trouble, but do not dispense with constant supervision on the part of the attendant, as they are somewhat liable to get out of order.

In England the usual way is, or formerly was, this: to employ only one jet of steam for each chamber, mostly beside, above, below, or even within the pipe conveying the gas from the burners, the Glover tower, or the preceding chamber. Some introduce the steam quite near the top, others in the centre of the chamber-end. A single steam-jet suffices, if the length of the chamber does not exceed about 130 ft.; in longer chambers it would not carry right through.

It is maintained by English practical men that a single steam-jet from a 1-in. pipe is quite sufficient for feeding chambers up to 130 ft. length, and also that the distribution of moisture through the chambers is thus properly effected. By arranging a single steam-jet, the cost of cocks, branches, etc., is saved, and the regulation of the supply of steam is much simpler and easier than if, for instance, four cocks were to be opened a quarter as much as the cock of a single jet. It is also true that in this way the front part of each chamber, which makes most acid and evidently requires the greatest supply of moisture, actually receives it; but this does not hold good of the first chamber, which obtains a considerable portion of its steam from the Glover tower, so that a steam-jet placed in the just described way is certainly not in the right position. The steam-jet should enter the chamber near the top, or at least in the upper part of the side. Experience has shown that it is not advisable to send the steam into the lower portion of the chamber.

Most experienced managers, however, now agree that the single steam-jet for each chamber is a faulty appliance. The chamber should not be left to haphazard supply of its different parts with the necessary amount of moisture, but each part should receive just what it needs.

On the Continent, indeed, most manufacturers have always preferred employing a number of steam-jets for each chamber, so as to make themselves independent of any casualties in the proper distribution of steam by a single jet. These branch jets are introduced at right angles to the direction of the gaseous current either in the long chamber-sides, not far from the top, or, which is most usual, through the roof of the chamber, so that the single jets can be regulated by a man walking over the top. Thus, for instance, at the Oker works there is a steam-pipe extending above the chambers, from which, at intervals of 17 ft., branches of ¾-in. bore enter the latter; from these the steam issues, by several small openings immediately below the top, in several directions (Bräuning, *Preuss. Zeitsch.*, 1877, p. 137). A similar arrangement exists at Aussig and elsewhere. In all these cases every branch-cock must be regulated separately.

Where a Glover tower is in use, the first steam-jet should not be in front of the first or "leading" chamber, as this part receives enough steam from the Glover tower; the first steam-jet should be 20 or 30 ft., or even farther, from the front side.

An apparatus by which steam can be introduced at many places and yet regulated at a single point has been described by Scheurer-Kestner (Wurtz, *Dict. de Chimie*, iii. p. 149); it is shown in Fig. 243: *a* is the copper main-pipe running in the centre of the chamber-top, and held fast by the joist b b_1, as well as the branches *c*. The latter are arranged alternately on the left and right hand at distances of 16½ ft.; they are made of lead, pass through the chamber-top, and are burnt into it. The arm *d*, covered with straw rope, serves for making the communication between *a* and *c*. Both pipes have hydraulic lutes, so that only a very low pressure can be employed. The main-pipe, *a*, is provided with a cock, and the supply of steam regulated by this. The steam, entering the pipe at the front end of the chamber, will principally escape through the first branches, where it is most needed, because in the beginning a large quantity of unchanged sulphur dioxide is present. The pipe *a* has sufficient fall for emptying the condensed water. (This arrangement seems to offer no advantage over simple branches on a main-pipe, and has the great drawback that only a very low pressure can be employed, as the water is easily thrown out of the hydraulic joints *a* and *c*. Moreover, it disregards the necessity of supplying the various parts of the chamber with different amounts of steam.)

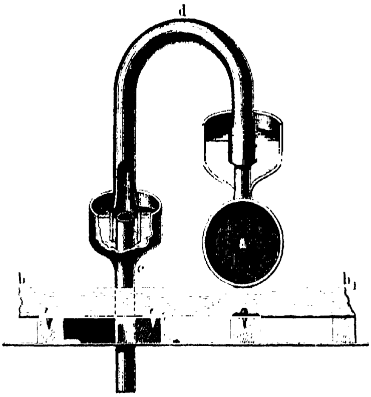


FIG. 243.

Perfectly absurd is the arrangement given in Payen's *Précis*, and copied from it into many other treatises. Here the steam-jets are shown partly in the chamber-bottom, coming through the chamber-acid. No practical man can imagine that this plan, if it has been actually carried out anywhere, has not been discontinued at the first opportunity; for the shaking by the steam must gradually cause a leakage at the joint, which cannot be got at, owing to the chamber-floor, nor can it be repaired till the chamber has been entirely emptied.

The total quantity of steam required for a set of chambers, which should be known approximately in order to fix upon the boiler-space and the size of the main-pipes, of course depends, first, upon the quantity of sulphur to be burnt, secondly upon the existence of a Glover tower, and thirdly upon the strength to which the acid is brought in the chambers. A general rule, therefore, cannot be laid down. The two latter conditions are partly reciprocal; the stronger the acid is made in the chambers, the less water is evaporated in the Glover tower, and *vice versâ.* If we assume, adopting a proportion very usual in England, that all the chamber-acid is brought up to 124° Tw., and that it is concentrated in the Glover tower up to 148° Tw., the amount of steam required will be as follows:—

Every pound of sulphur burnt requires,

1st, for forming $\frac{98}{32}$ SO_4H_2, $\frac{18}{32}$ water . = 0.5625 lb.

2nd, for diluting it down to 124° Tw.

(= 70 per cent. SO_4H_2), $\frac{30 \times 98}{70 \times 32}$. = 1.3125 „

1.8750 „

Of this nothing is lost with the escaping gas, as this passes in the Gay-Lussac tower through strong vitriol; on the contrary, the Glover tower saves the steam corresponding to a concentration from

124° (= 70 per cent.) to 148° Tw. (= 80 per cent.), viz., $\frac{10 \times 98}{70 \times 32}$ . . = 0.4375 lb.

Leaving . . . 1.4375 „

which must be supplied to the chambers. To this must be added a certain quantity for water condensing in the steam-pipes; but this cannot be estimated generally, since here everything depends upon the length of the pipes, their thickness, surroundings, etc. On the Continent the chamber-acid is kept more dilute and correspondingly more steam is used. It is safe to say that the steam to be generated in the boiler, without a Glover tower, amounts to about two and a half times—with it, to about twice the weight of sulphur burnt.

Introduction of Water in the form of Spray.

Instead of feeding the chambers with steam, Sprengel (B. P. of 1st October 1873) proposed to employ liquid water in the form of a fine spray. His reasons are these:—that the steam increases the volume of the gases by its heat, and consequently more chamber-space and nitre are required, which can be avoided by introducing the water in a liquid form, sufficiently divided; and that the cost of evaporation can be saved in this way. The water is made into a spray by the employment of steam, a steam-jet of 30 lb. tension escaping through a platinum nozzle in the centre of a water-jet, as shown in Fig. 244 (where *a* is the steam-pipe, *b* the water-pipe); 20 lb. of steam is sufficient for converting 80 lb. of water into a mist. Such jets are arranged in the chamber-sides, at distances of 40 ft. apart, and supplied with water from a tank fixed at some height above. Sprengel assumed that two-thirds of the coal can be saved in this way, instancing the works at Barking Creek, where at the same time a saving of 6½ per cent. pyrites and of 14¾ per cent. nitre is said to have been effected. At those works there was no Gay-Lussac or Glover tower. In the case of factories working with a Glover tower, Sprengel estimated the saving in coal at a third less (*Chem. News*, xxxii. p. 150). Of course the water- and steam-cocks must be exactly regulated, and the two nozzles must have a particular shape, so that only a fine mist and no larger drops shall be formed, which would at once fall to the bottom and only dilute the chamber-acid.

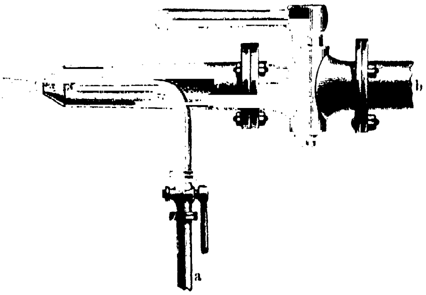


FIG. 244.

A different way of producing a spray or mist of water instead of a steam jet for feeding vitriol-chambers is employed at the Griesheim works, and has thence been introduced with great success into several other factories. The spray is there not produced by the injection of steam, but by allowing the water to issue at a pressure of 2 atm. from a small platinum jet against a small platinum disc. Two rows of such water-jets are introduced through tubes in the chamber-top, each tube about 20 ft. away from the other. Thus the whole chamber is uniformly filled with a fine mist, which, together with the steam coming from the Glover tower, supplies all the water required for the chamber-process. The water must be carefully filtered, as otherwise the jets would soon be stopped up; but this trouble is far more than compensated by the considerable saving in fuel caused by doing away with the chamber boilers. The fear formerly entertained, that the introduction of the moisture in the shape of liquid water would reduce the temperature of the chambers below that most favourable for the acid-making process, is entirely groundless. At Griesheim it was noticed that the temperature of the gases, arriving from the Glover tower sometimes at only 35° C., quickly rose within the chambers to 50° C. Similar observations have been frequently made, most extensively by Lunge and Naef (*cf.* Chapter VII.). This is explained by the fact that the evolution of heat, consequent upon the chemical reactions going on within the chamber, is far more important than the heat brought in by the steam, and that, in fact, the local cooling produced by the water being supplied in the liquid form is actually beneficial in most cases.

It might be objected to the introduction of the water in the shape of a spray, that steam is preferable on account of being only gradually condensed in its onward course within the chamber, and that the moisture would thus be more uniformly distributed through the chamber. But this objection is not at all valid, and would not be so even if no sulphuric acid were present in the chamber. Calculation shows that the gas introduced for each kilogram of sulphur, whose volume at 50° C. and 760 mm. pressure amounts to 8345 l., can contain only 0·6868 kg. of aqueous vapour, whilst the total amount of water is nearly four times as much, and three-fourths of the steam entering into the chamber must therefore be at once condensed into water. This calculation, given in our first edition, pp. 348 and 349, is not repeated here, since it does not take into account the fact that the tension of aqueous vapour within the chamber is very much reduced by the presence of sulphuric acid, and it is hence useless for our purpose. Hurter (*J. Soc. Chem. Ind.*, 1882, p. 51) somewhat more correctly applies to our case Regnault's table for the tension of aqueous vapour in sulphuric acid of various strengths, and he there gives a diagram which allows of finding this tension for any intermediate concentration of acid. But this is incorrect for the principal working part of the vitriol-chamber; for Regnault's determinations only go as far as 35° C., that is much below the ordinary chamber-temperature, and it is not admissible to calculate tensions at 60°, 80°, or even higher temperatures by simply applying Regnault's table or Hurter's diagram to them. This gap has been filled by a set of elaborate observations made by Sorel, and first rendered accessible to the public by me (*Z. angew. Chem.*, 1889, p. 272). Sorel's table extends to acids from 44 to 82 per cent. H_2SO_4, and to temperatures from 10° to 95°. We have given it in Chapter III., p. 312, where the specific gravities corresponding to the acid percentages have been added for the reader's convenience. At the close of this chapter we shall give a table for reducing volumes of gases to the conditions of the vitriol-chamber atmosphere, which equally takes into account the aqueous-vapour tensions of sulphuric acids of various strengths.

The importance of this table will be indicated at present by only one example. In a special instance the temperature close to the chamber-side was 80°; the acid running down the side stood at 114° Tw. = 66 per cent. H_2SO_4, and the aqueous-vapour tension at this place was, therefore, = 39 mm. Only 6 c.c. (say 2½ in.) within the chamber the temperature was already 95°; but at this temperature an acid, whose aqueous-vapour tension is = 39 mm., must have a strength of 128½° Tw. = 72·33 per cent. H_2SO_4, and this was found to be really the case. We shall see the importance of this in Chapter VII.

Looking at the great reduction of the tension of aqueous vapour by the presence of sulphuric acid, we must conclude that the steam introduced into the chamber must be condensed almost immediately into a liquid mist, and this must reduce the alleged superiority of steam in "carrying power" to a properly comminuted spray of water, introduced at high pressure, to almost *nil*.

Of course the water *must* be properly comminuted; otherwise, that is when it drops from the jets in the shape of rain, it dilutes the chamber-acid to an intolerable degree, and this is all the more injurious as this dilute acid floats on the top of the stronger chamber-acid, and is not noticed for a long time at the places where the acid is drawn off, till it becomes too late to meet the evil at once. This accident will happen whenever the jets are out of order, and this has, very unnecessarily caused several works to abandon the plan of introducing the water in the shape of a liquid spray.

A special platinum jet for converting water or acid liquids into a thin spray has been constructed by F. Benker, of Paris, and is shown in Fig. 245. In this jet the distance between the nozzle *a* and the disc *b* is adjustable, the disc being moved backwards or forwards by means of a rod, at the end of which is cut a fine thread, which works in a similar nut *c*, placed on the top of the cylinder. The screw and nut are made of an alloy of platinum and iridium, so that there is no fear of their wearing out. In this manner the best distance between *a* and *b* can be easily attained, and by removing *b* altogether the nozzle *a* is easily cleaned. More recently Benker has employed spray-producers of the shape shown in Fig. 246, with the platinum-iridium jet cased in antimony-lead, and without an adjusting-screw.

Körting Brothers' spray-producer (Fig. 247) (*Z. angew. Chem.*, 1888, p. 404) contains within the contracted part a metal spiral, which by the pressure of the liquid is kept tightly in its place, whilst the liquid on passing through the helicoidal channel takes

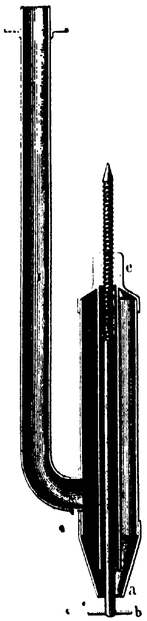


FIG. 245.

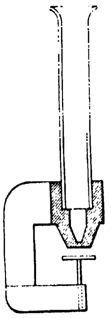


FIG. 246.

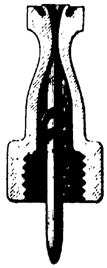


FIG. 247.

a rotating movement, so that, on issuing, it is projected equally on all sides as a conical spray. The nozzle and spiral spring can be arranged for spray of any degree of fineness. This apparatus was originally intended for damping the air in cotton-mills, etc., for precipitating dust, for absorbing acid vapours, and so forth. It has also been made of platinum, and is in several places used for producing a fine spray of water in vitriol-chambers.

These Körting's spray-producers ("Streudüsen") were also made of antimony-lead with a platinum lining, but this did not stand the corrosion in acid-chambers, and had to be replaced by solid platinum nozzles. Even these do not last so long as nozzles made of glass, as shown in Fig. 248. The glass tube *a* is drawn out to a capillary point at *a'*, where it is cut off quite straight so that the jet of water comes out centrally, not sideways; in twenty hours 900 or 1000 l. of water should be delivered from this. This glass nozzle is fixed in the antimony-lead part *d* by means of a thin india-rubber washer *b*, the joint being made tight by the water pressure, and both orifices being at the same level. Within *a* the Körting spiral *e*, made of gun-metal (this metal can be employed, as no acid penetrates here), is fixed by the thick india-rubber tube *c*. This apparatus is set in the chamber-top in such a way that the jet comes out horizontally, and that the whole can be removed at will for the purpose of cleaning or inserting a new glass nozzle.

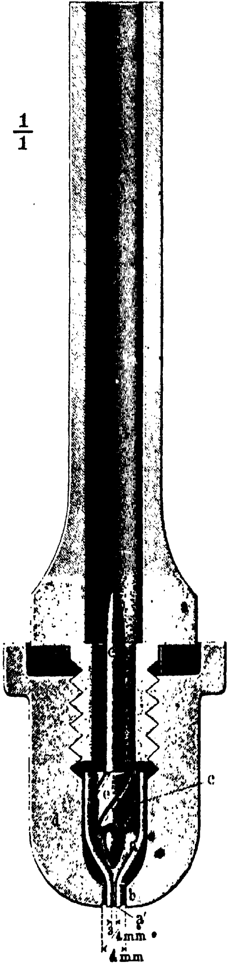


FIG. 248.

In practice the orifice of the glass tube *a* is about 0·75 mm. bore, that of the hard-lead nozzle *d* is 4 mm. wide. In order to fix *a* in the hard-lead part *d*, the small india-rubber washer *b* is put on and placed with its orifice at the top, and *d* is put on with a twisting motion, but without exercising much pressure or trying to centre *a* exactly in *d*, the water pressure afterwards accomplishing this much better. With a pressure of 3 to 5 atm. and a properly adjusted nozzle no droplets whatever are formed, but a uniform mist travelling over a great distance. The Körting spray is bought in the ordinary way, and is fitted at the works with a glass jet, as shown here with every detail.

Glass-nozzled spray-producers, precisely as here shown, have been employed for many years at one of the best conducted continental factories, and are still preferred there to every other form of apparatus of this kind. Since their introduction all previous trouble in feeding the chambers with liquid water has disappeared. The orifice of the glass jet has ¾ mm. bore, that of the hard-lead nozzle 4 mm. bore. Jacobs, in his Ger. P. 141453, describes a special spray-producer for lead-chambers. Guttmann (*J. Soc. Chem. Ind.*, 1903, p. 1333) and Falding (*Min. Ind.*, 1901) strongly recommend the use of a water-spray in lieu of steam in the acid-chambers.

During the warmer portion of the year the whole of the chambers can in any case be supplied with water as a spray; but in the winter season in some places the back part of the system must sometimes get a little steam.

For all descriptions of spray-producers the water must be carefully *filtered*, preferably by means of sponge-filters. Benker, moreover, places wire-gauze in front of every spray-producer. He works these at a pressure of from 2½ to 5 atm., by means of a small intermediate cylinder, about 3 ft. wide and 6 or 9 ft. high. For the first start a little high-pressure air is employed; afterwards the feed-pump gives sufficient pressure, which can be reduced by means of a tap if too much water is discharged.

This plan is very well illustrated by Figs. 249 and 250 (folding-plate), which at the same time show a chamber as erected by Mr Benker for the "intensive production" or "high-pressure style" (pp. 639 *et seq.*). A is a small air-pump, B the water-pressure vessel, made of an old steam-boiler, with two safety-valves, *a* and *b*. One of these, destined for the air, is very small; but the other, for the water, must be large enough to discharge the whole of the water supplied by pump D; otherwise B might burst. The second valve is weighted ½ atm. more than the air-valve. The level of the water in B must be kept 12 in. below the top. Pump D is an ordinary feed-pump, kept continuously going; between B and D is interposed the sponge-filter C. The water rises in the high-pressure pipe EE to the top of the chamber, where there are taps, *c c*, at distances of about 16½ ft. Behind each tap is placed a leaden filter (shown on a larger scale in Fig. 251), with a very fine wire-gauze sieve; then comes a swan-neck pipe, which passes through the chamber-top, and this ends in a spray-producer, Fig. 246 [or else 248]. From time to time the air-tap on B is opened in order to replace the air dissolved by the water under the high pressure. Kestner (*J. Soc. Chem. Ind.*, 1903, p. 344) strongly recommends this apparatus.

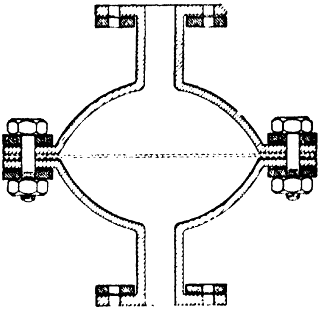


FIG. 251.

Rabe (*Z. angew. Chem.*, 1906, p. 2079) describes a controlling apparatus for spray-producers in the chambers, consisting of a glass tube, interposed in a suitable place of the entrance pipe, in which tube is placed a glass ball, which takes a higher or lower position, corresponding to the quantities of water flowing through the tube. A tap in the same place admits of regulating the corresponding tuyere. In this way the whole of the spray-producers of a set of chambers may be regulated from a single place, without checking each individual spray.

Gaillard (B. P. 11732 of 1908) describes the arrangement of conical extensions in the roof of the chamber, to increase the height of the nozzle of the spray-producer; a tray is placed underneath to convey any water entrained in a coarser state away from the chamber, instead of diluting the chamber-acids.

Scherfenberg and Prager (Ger. P. 219789) supply the water required for the chamber-process, by spraying it upon undulated, perforated surfaces inside the chamber. Before the water arrives at the bottom, it is converted into sulphuric acid. By this means the chamber-space is much better utilised, similar to reaction towers. In the cooler back part of the chambers steam may be used in lieu of water, as it here condenses at once, and the higher temperature thus produced is useful. In lieu of water, dilute acid may be used for this purpose.

Delplace (Fr. P. 342117) washes cooled burner-gases with strong sulphuric acid, in order to take out any SO_3 present, compresses them, and then applies them to injectors by which the water for the chambers is converted into a spray.

Fig. 252 shows the spray-producers model of 1909, as now preferred by Koerting Brothers. They produce a flat, horizontal spray, and are made of acid-resisting metal. They are placed in the hydraulic seal, A, which is otherwise closed by the cover, B, and are put in their places only when the chamber is already at work. They are left in action when taken out for revision, and are joined to the water-main by lead piping. In order to prevent their being stopped up too soon, a gravel- and sponge-filter is interposed in the water main.

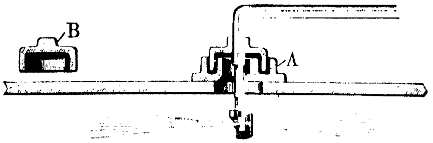


FIG. 252.

A. Primavesi, of Magdeburg (*Chem. Zeit.*, xxx. p. 300), supplies low-pressure spray-producers with an ebonite nozzle.

Schutte and Koerting, in Philadelphia, make spray-producers with glass-nozzles.

A special advantage of the introduction of liquid water in the form of spray is that the temperature of the chambers is kept lower than when employing steam, since the latent heat of the latter, which becomes free in its condensation, does not come into play. How useful such a cooling effect is, will be seen in Chapter VII. The only drawback to the spray system is the liability of the orifice of the spray-producer to get choked up by dirt, or else to be widened by corrosion. The former is avoided by careful filtration of the water, the latter by a suitable construction. Glass nozzles, as shown above, are much better even than platinum. I have found this system applied for many years with full success in a number of the best managed works, *e.g.* Griesheim and Aussig. Wherever it has proved unsuitable, this has been due to want of attention.

Benker and Hartmann (*Z. angew. Chem.*, 1903, p. 864) make the following calculation. Each gramme-molecule of SO_3, (64 g.) according to Lunge's calculations, on its conversion into $H_2SO_4,3H_2O$ (which is the approximate composition of chamber-acid) liberates 65,500 calories. These 64 g. SO_2 require for their conversion into sulphuric acid of the above strength 72 g. water. Each gramme steam, introduced into the chamber (at 60°) with a temperature of 120°, yields $606{\cdot}5 (0{\cdot}305 \times 120) - 60 = 583$ cal. Hence the total heat evolved is: $65500 + 583 \times 72 = 107{,}476$ cal. If, however, the water is introduced in the liquid state at 15°, it must be heated up to 60°, and that amount, $72 \times 45 = 3240$ cal., must be deducted from the 65,500 cal., leaving but 62,260 cal., or a difference of 45,216 cal. against the case of steam. But it is not possible in all cases to feed the chambers exclusively with sprayed water in lieu of steam; especially during the winter months a certain amount of steam must be employed, in order to prevent the temperature from going down below a certain minimum. That minimum is 60° to 65°; the difference between the temperature of the [first] chamber and the outer air must not be essentially below that amount. Where the chambers are driven slowly, only little sprayed water can be employed. The saving of coals by replacing the 500 kg. steam, required for 1000 chamber acid, by liquid water, may be put at 75 to 100 kg.—Those views have been later on discarded by their authors; in a paper published in *Z. angew. Chem.*, 1906, p. 135, Hartmann and Benker now insist on the *total* exclusion of steam from the chambers.

In the *42nd Report on Alkali Works for* 1905, p. 17, we find the following passage:—"The testimony as to the advantage of replacing steam by water sprays in the earlier chambers of a series is decidedly conflicting. In some works, where a long trial has been given, their use has been abandoned. Success depends upon the observance of minute and exact precautions that are necessary for ensuring the constant supply of the requisite quantity of water without liability to interruption. Moreover, it is only in the earlier chambers of a series that steam can be replaced by atomised water, since in the back chambers, especially in the winter season, presence of steam is necessary to maintain a suitable temperature for continuity of reaction among the gases." The 43*rd Report for* 1906, p. 24, on the other hand, gives a very favourable account of the entire replacing of steam by water-spray in a factory where there was a certain amount of irregularity in the work.

Dilute sulphuric acid, e.g. from the last chamber, instead of pure water, is used for the introduction into the chambers by spray-producers by several inventors, *e.g.* Guttmann (B. P. 18927 of 1906), Rabe (*Z. angew. Chem.*, 1910, pp. 8 to 12), Scherfenberg u. Prager (*suprà*, p. 736), etc.

Production of the Draught in Vitriol-chambers.

The draught necessary for working acid-chambers is produced by various agencies, the most important being the high temperature with which the gases leave the burners and enter the chambers, which counterbalances the greater density of the burner-gases when compared with that of air in the cold state. We shall calculate these factors for the various cases in question, employing the following values for the density of gases and vapours at 0° C. and 760 mm. mercurial pressure[1]:—

	grammes.
1 l. of dry atmospheric air weighs	1·2932
1 „ oxygen „	1·4298
1 „ nitrogen „	1·2562
1 „ sulphur dioxide „	3·8721
1 „ aqueous vapour „	0·804343

We shall begin with *burner-gases from brimstone*, the normal composition of which has been calculated (pp. 536 *et seq.*) = 0·1123

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[1] The litre-weights employed differ slightly from the more recent values, given, *e.g.*, in my *Technical Chemists' Handbook*, 1910, p. 16, but it did not seem worth the while repeating all the calculations, as the practical conclusions drawn from them remain entirely unchanged, the deviations of the figures being quite immaterial.

$SO_2+0{\cdot}0977\ O+0{\cdot}7900\ N=1$ l. of gas. This must weigh at 0° and 760 mm. pressure:

$$0.1123 \times 2.8731 + 0.0977 \times 1.4298 + 0.7900 \times 1.2562 = 1.4547 \text{ g.}$$

Taking the temperature in the outlet-pipe from the brimstone-burner to average 100° C. (which is much below the actual temperature), the above 1·4547 g. would occupy a space of $\frac{273+100}{273}=1{\cdot}3663$ l., or 1 l. of the burner-gas at 100° C. and 760 mm. $=\frac{1{\cdot}4547}{1{\cdot}3663}=1{\cdot}0647$ g.

Atmospheric air at 0° and 760 mm. pressure weighs per litre 1·2932 g.; at 20° this quantity occupies the space of 1·0733 l., at 35° = 1·1282 l., so that even at the highest summer temperature, say 35° C., 1 l. of air weighs as much as $\frac{1{\cdot}2982}{1{\cdot}1282}$ = 1·1463 g.; it is therefore in any case heavier than the burner-gas at 100° C.

The aqueous vapour always present in the air need not be taken into account, since by its expansion in the heat of the burner it can only increase the difference between the weight of the gas and that of the air.

Owing to the fact that the gaseous mixture in the vertical pipe of the sulphur-burner is lighter than air, it must issue out of the top of the pipe into the chamber with a speed corresponding to the excess pressure of the atmosphere acting upon it from below. It must therefore by itself exercise a pressure upon the gas in the lead chamber. Its speed or the draught increases with the height of the vertical pipe; and the latter therefore ought to enter the chamber-side as high up as possible. By thus providing more than sufficient drawing power, the supply of air is assured in any case; and its excess can always be moderated by narrowing the area of the inlets.

A second cause of draught is the formation of sulphuric acid itself, as the space occupied by the consumed gas cannot remain empty, and must at once be filled again. The condensation of the gas to sulphuric acid thus acts as an aspirator.

A third cause of draught is the vertical pipe taking the gas away from the last lead chamber or the chimney with which it is connected. As the gas in these contains all the nitrogen introduced into the chambers with only 5 per cent. of oxygen (a mixture of 95 vols. N+5 vols. O has the litre weight gr. 1·263; ordinary atmospheric air 1·293), as it is saturated with aqueous vapour, and as it is usually warmer and never can be colder than the atmospheric air, it must necessarily be lighter than the latter; this is evident without any calculation.

If the nitrogen-acids are not recovered by a special process, to be explained later in the next chapter, the gas certainly contains a little of those acids and of sulphur-dioxide, by which its specific gravity is somewhat increased. We shall, however, see that their effect is very slight, and does not materially interfere with the causes producing the draught.

The draught produced by all the above-mentioned causes regulates the quantity of air which can enter the apparatus by openings of a certain size. We have already seen, on p. 556, that we must not introduce the exact quantity of air required for transforming the burnt sulphur into SO_3, but a certain excess, which we have calculated = 5·18 vols. of oxygen upon each 14 vols. of SO_2. With this, for each 14 vols. of SO_2,

$$\begin{aligned} 14+7+5.18 &= 21+5.18 = 26.18 \text{ vols. oxygen,} \\ \text{and } 79+19.50 &= 98.50 \text{ ,, nitrogen,} \\ \hline \text{together } & 124.68 \text{ ,, atmospheric air,} \end{aligned}$$

must be introduced into the chambers. From this it follows that for each vol. SO_2 $\frac{124{\cdot}68}{14} = 8{\cdot}906$ vols. of air are required. Now 1 l. of SO_2 at 0° and 760 mm. pressure weighs 2·8731 g., and SO_2 consists of equal parts by weight of sulphur and oxygen. Accordingly 1 l. of SO_2 at 0° and 760 mm. contains

$$\frac{2.8731}{2} = 1.43655 \text{ g. sulphur,}$$

$$\text{and } 1.43655 \text{ g. oxygen.}$$

Thus for each 1·43655 g. of sulphur burnt 8·906 l. air at 0° and 760 mm. are required. Since

$$1.43655 : 1000 :: 8.906 : x$$

each 1000 g. or 1 kg. sulphur requires $\frac{8906}{1{\cdot}43655} = 6199$ l. air at

0° and 760 mm. pressure to be introduced into the sulphur-burner, weighing 6199 × 1·2932 = 8017 g. or 8·017 kg.

At 20° C. this weight would occupy $\frac{273+20}{273} \times 6199 = 6653$ l.

All these calculations refer to *dry* air. If the air is saturated with moisture, its volume is increased by the vapour-tension e for the temperature in question, according to the formula:

$$V_1 = \frac{V \times 760}{b - e},$$

where b is the actual barometric pressure. At 20° C., e is = 17·4 mm., and for $b = 760$ the above 6653 l. will be = 6809 l., if saturated with moisture.

The last increase of 156 l. is only fully realised in the exceptional case of air completely saturated with moisture. As this increase is only 2·34 per cent. of the volume of the necessary dry air, whilst, according to the calculation on p. 557, nearly 25 per cent. of the theoretical quantity of air (that is, more than ten times as much) is introduced in excess, the changes in the moisture of the air and the differences of volume resulting therefrom are of no practical consequence. We shall therefore not enter into a calculation of the differences caused by the real percentage of moisture in the air.

In the case of *pyrites-kiln gases*, it follows, from the data given on p. 558, that for each 100 parts of sulphur employed as FeS_2,

375 parts oxygen must be supplied for oxidising the Fe,
1000 „ „ „ forming SO_2,
500 „ „ „ oxidising this to SO_3.

Since 1 l. of air at 0° and 760 mm. pressure weighs 1·4298 g., at this temperature and pressure

375 g. O give 262·3 l. mixed in the air with 986·7 l. N.
1000 „ „ 699·4 „ „ „ 2631·1 „
500 „ „ 349·7 „ „ „ 1315·5 „
1875 „ „ 1311·4 „ „ „ 4933·3 „

Theoretically, then, for each kilogram of sulphur consumed as FeS_2, 1311·4 + 4933·3 = 6244·7 l. air at 0° and 760 mm. pressure must be supplied.

The normal pyrites-burner gases, as calculated, p. 559, contain

8·59 per cent. by vol. SO_2, 9·87 O, and 81·54 N (not reckoning any SO_3 present).

1 l. of this gas at 0° and 760 mm. weighs

$$0.0859 \times 2.8731 + 0.0987 \times 1.4298 + 0.8154 \times 1.2562 = 1.4122 \text{ g.}$$

whilst the 1 l. of the gas resulting from the combustion of brimstone, according to our former calculation, weighs 1·4547. The former being, under equal conditions, lighter than the latter, consequently gives stronger draught.

Of course the volume of air necessary for a certain consumption of sulphur is also dependent upon the elevation of the site above the level of the sea, which regulates the mean barometrical pressure. Thus at Munich a quantity of air will occupy a space larger by 5·5 per cent. than the same quantity at Widnes or New York.

It is easy to introduce the minimum of air required for proper work. But this is not all; an excess of air is just as injurious as a deficiency, although not to the same extent. Air in excess cools the gas, and thus may sometimes interfere with the process; it fills a portion of the chamber-space and renders it inoperative; it dilutes the gas and weakens the energy of the chemical action. The regulation of the supply of air must therefore be accurate, and must be adapted to the frequent variations in the state of the atmosphere. This must be done by great attention in enlarging or diminishing the openings serving for introducing the air and for taking away the gas. In both of these ways the supply of air can be diminished; but it is not indifferent which of them is selected. By the latter the draught acting upon the contents of the chambers at the end of the apparatus, by the former the pressure upon the contents of the chambers at the beginning of the apparatus, is lessened. With the latter method the pressure inside the chambers is increased; with the former it is diminished. Accordingly, if the chimney-draught is too much cut off, the gas issues forcibly from any openings in the chambers, etc., whilst the air may enter properly by the holes in the front of the sulphur-burners. If, however, these latter are stopped up too far, the chambers suck in air in any places not completely closed against the atmosphere.

The draught may also be increased in two different ways, viz., by enlarging the opening in the exit-tube, or by increasing the inlet-holes in the door of the burner. Then the chambers, if the exit-tube is not sufficiently closed, suck in air; if, on the other hand, the inlet-openings are too wide, gas is forced out from any leaks in the chambers by the excess pressure. This is especially noticed when the doors are opened for charging. Both faults can be avoided by arranging a certain proportion between the inlet and the outlet openings. Usually the area of the latter is two-thirds that of the former. For the changes of draught made necessary by the variations in the state of the atmosphere no certain rules can be given; observation and practice must come into play here. In well-arranged works, however, this is not left to chance, but the supply of air is checked by regularly estimating the oxygen in the escaping gas, as we shall see later on.

We have thus seen that the hot gaseous mixture in itself contains the conditions for causing a draught, since it is much lighter than the air, and will always have a tendency to rise from the burners to the chambers. We must also point to the second source of draught, viz., the formation of liquid sulphuric acid within the chambers from the mixture of the gases, which must necessarily have an aspirating action, although not only from the burners, but from all sides.

Together with these two sources of draught furnished by the peculiar nature of the acid-making process itself, there must always be another arrangement for causing further draught, especially because otherwise the current of gas could not be turned into the required direction. In the simplest case a plain *outlet-pipe* behind or above the last chamber will suffice. The Belgian Commission of 1854 even preferred this arrangement to a chimney, because the latter might produce an excessive draught; and many factories work quite well in this way. But it cannot be said that the excessive draught of a chimney must lead to a loss of uncondensed gas and too quick a passage through the chambers; for it is always very easy to cut off an *excess* of draught by a damper, etc., in the outlet; but it is nothing like so easy to increase the draught in the outlet-pipe or chimney if *insufficient*. For the latter object a *steam-injector* placed in the outlet-pipe was formerly considered the most convenient apparatus. Sometimes, in lieu of a proper injector, a simple steam-jet, turned in the direction of the draught, is employed; but this is a very wasteful proceeding, and a proper Körting's injector, made of regulus metal (lead and antimony), should always be employed. Such injectors can be applied in various places. Scheurer-Kestner (*Bull. Soc. Chim.*, xliv. p. 98) describes his experience in this direction. He employed a Körting's injector which produced a gaseous mixture of 7·9 per cent. steam and 92·1 per cent. air. Thus a quantity of 1814 kg. of water in the shape of steam sufficed for aspirating the air required for burning 7000 kg. of 45 per cent. pyrites. At first the injector was placed in the pipe entering into the first chamber. This is the best place, where there is no Glover tower, as the steam used in the injector also serves for working the chambers, and thus costs nothing; but in case of a Glover tower this produces an excess of steam in the first chamber. The regulus metal of the injector in his experiments wore out pretty quickly; nor could it be replaced by porcelain, which cracked very soon; a thin casing of platinum, however, was found sufficient for protecting a regulus injector. It was tried to place the injector between the first and second chambers, but here also too much steam was introduced into the chamber. This is avoided by applying the injector at the exit from the Gay-Lussac tower; but then all the steam is lost and the process is thus made expensive. In the case of seleniferous pyrites the injector between the burners and the chambers is stopped up so quickly by a deposit of selenium, that two injectors must be employed side by side, one of which can be cleaned out while the other one is going.

Steam-injectors between the Glover tower and the chambers are, as we see, impracticable. This holds good of any place in the system, except in the exit-pipe or chimney itself. But in the chimney where the steam cannot be utilised for the chamber process, they cause considerable expense.

Chimneys.—It must not be overlooked that in the case of employing steam-injectors a regulation is all the more called for, lest the draught should be too strong; and in the end a cheap source of draught, viz., the chimney, has been replaced by a dear one, without any gain as to constant supervision and regulation. We should accordingly in ordinary cases prefer a *chimney* to a steam-jet, all the more as the former will always be necessary in any case for the steam-boilers. Of course the chimney, to do its work, must be higher than the chambers.

Where a chimney cannot be employed for one reason or another, nothing remains but to have recourse to a mechanical contrivance (fan-blast), as will be described below.

It answers much the same purpose as a chimney if the outlet-pipe fixed to the last chamber has a considerable height —for instance, 50 ft. (as is the case in the south of France). Where several sets of chambers exist in the same works, it is preferable to carry them all into a common chimney, providing the connecting-pipe of each set with a contrivance for regulating the draught. It is not a good plan to utilise for the chambers a chimney with which ordinary furnaces are connected, as the draught will be of a very variable character in this case, and the working of the chambers will not be easily kept entirely regular. Still, at some works this plan cannot be avoided, and must be provided for by more careful regulation of the draught. In such works more than anywhere else the automatically acting dampers, described below, are recommended to be used.

The employment of a chimney is even more advisable if, as is now the case in all well-appointed works, a Gay-Lussac tower is placed at the end of the set. In this case the draught must be regulated with even greater care than otherwise; but there must be an excess of draught at disposal to begin with. It is also a great improvement if the "sight" necessary for checking the work of the tower (*cf.* Chapter VI.) can be arranged in the down-draught near the ground-level, or at least the gangway round the chambers. If there is no down-draught, but a direct top-draught out of the tower, it is always necessary to mount to the top to observe the "sight." It is certainly quite possible to employ the tower itself as a chimney, if it is built with its top a good deal higher than the chambers; and this is actually done at a good many works, but probably in some cases only because there is no chimney available. The drawbacks of this plan are well illustrated by the following passage from the official *Alkali Reports*, No. 21 (for 1884), p. 74:—"No. 2256. The vitriol-exit from the plant in which the pyrites-smalls are burnt used to be at the top of the Gay-Lussac tower. I found an exceedingly high escape from here on my first three visits. The manager has since connected this exit to the main chimney, and now finds he can better regulate the draught in his chambers. Since this has been done the tests have been invariably good."

The chambers at Oker, utilising the configuration of the ground, are arranged in such a way that the burners, Glover towers, chambers, and Gay-Lussac towers rise one above the other, terrace-wise. The outlet of the whole is at a height of 62 ft. above the level of the burner-grates. Drawings of this arrangement are given by Bräuning (*Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen*, 1877, Table II.). It is stated there that formerly the draught could not be made sufficient, even by connecting the Gay-Lussac towers with the boiler-chimneys.

I have received the following notes concerning the Oker system during 1902:—A set of chambers, started in October 1883, was formerly connected by a 2-ft. pipe from the Gay-Lussac towers with the steam-boiler chimney. The draught was good, but the chimney, made of common bricks, suffered very much. Since 1896, when the chimney became superfluous through the centralisation of the boiler plant, the gases have been passed straight out of the Gay-Lussac tower in all five sets of chambers. The draught is quite sufficient, without any artificial help; but this is easy to understand from the conditions described above. There is also the convenience of running both the chamber-acid and the Gay-Lussac acid into the Glover tower by natural fall.

It has been noticed at Oker that a very long draught-pipe, connecting the last chamber with the tower, has the advantage of neutralising to some extent the oscillations of the outer atmospheric pressure, and thus facilitating the regulation. Be this as it may, such a long pipe, although it causes some loss of draught by friction, will always be very useful, by cooling the gas previously to entering the absorbing-tower. The same has been found at the Stolberg works (1902).

Very frequently one chimney has to serve two or more sets of chambers. It is perfectly well understood, from innumerable analogous cases in ordinary firing operations, that, where several apparatus are served by the same chimney, special care must be taken that they receive the same amount of draught. Wherever possible, the main flues are taken separately to the chimney and are introduced into the latter in such a way as not to interfere one with another, which can be attained by erecting mid-feathers within the chimney. Where it is necessary to connect several sets of chambers with the same main flue, it must not be overlooked that the draught is stronger in the part nearer than in the part farther removed from the chimney; by suitable arrangement of the dimensions, by avoiding sharp angles in the places where the branches form the main flue, by mid-feathers, and by regulation by means of dampers, a proper equalisation can generally be attained.

Other arrangements.—Sometimes none of the ordinary measures secure an equal draught for two sets of chambers, even when the flues from these meet about the same distance from the chimney. In such cases it is best to make the individual flues end in a large chamber, from which starts the main flue leading to the chimney, and to fill this chamber loosely with bricks, of course not to such an extent that the draught is too much restricted. This produces numerous small and constantly changing currents, which prevent any one of the large currents getting the advantage of the others, and thus equalises the draughts.

C. L. Vogt has patented (B. P. 29th July 1875) a peculiar contrivance for producing draught in acid-chambers, which introduces the air together with the necessary steam through a pipe with an opening of ¼ in. The steam is under a pressure of 3 to 4 atm. Sorel (*Fabrication, etc.*, p. 291) states that this had been practised in France twenty years earlier. Such a contrivance is only exceptionally called for; but there are cases in which a supply of air behind the burners seems desirable (Chapter VII.).

At some factories they work in this way: the Glover tower is packed very loosely, and itself acts as a chimney, so that the burners have always very good draught and never blow out, whilst it is quite possible at the same time to keep the exit draught so low that there is some little outward pressure even in the last chamber. In the next chapter we shall describe an arrangement by which this aim can be attained even more perfectly.

Regulation of the Draught.—We have already said something about the principles according to which the supply of air must be regulated ; and we shall have to return to this in the next chapter. Here we can only remark that there must be in any case enough total draught *behind* the chambers, but not too much; otherwise, even if the burners themselves are protected against excess of draught by diminishing the air-holes below the grates, there is all the more tendency for air to enter the chambers from all other sides through the finest chinks and thus disturb the process. If the draught is excessive, the incubus of the vitriol-maker, pale chambers, at once makes its appearance.

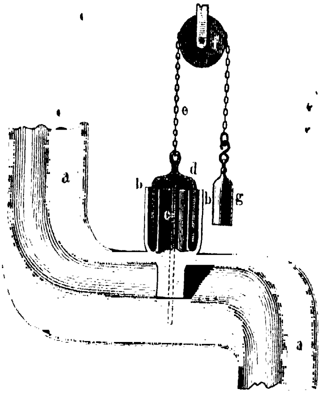

FIG. 253.

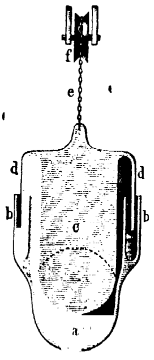

FIG. 254.

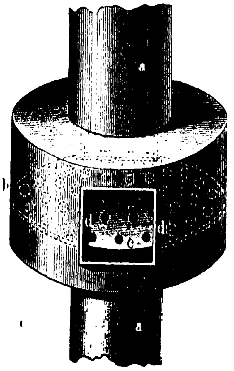

FIG. 255.

Whether, therefore, the draught is produced by a chimney or by an open pipe, there must always be some contrivance *for regulating* it. At many works this is done by a simple damper, introduced into the respective lead pipe by a slit, luted with clay or not at all. The arrangement shown in Fig. 253, partly in elevation, partly in section, and in Fig. 254, in cross section, is far more perfect. The draught-pipe, *a a*, is widened out into a rectangular vessel surrounded by a jacket, *b b*, forming a hydraulic joint; and the damper, *c*, is surrounded on all sides by the jacket *d d*, dipping into the water-lute at *b*. The damper is raised and lowered by the help of the chain, pulley, and balance-weight, *e*, *f*, *g*.

In continental works the arrangement shown in Fig. 255 is frequently met with. The draught-pipe, *a a*, is interrupted by a wider drum, *b*, divided into two parts by a horizontal diaphragm, *c*. The latter is perforated by a number of holes whose total area is somewhat larger than that of the pipe, *a a*. When, therefore, all the holes are open, there is no obstacle whatever to the draught; but this can be produced at will by closing a certain number of the holes with clay or lead plugs. For this purpose the space above the diaphragm is accessible by a small door, which may consist of a pane of glass, *d* (Fig. 255), to which another pane on the other side corresponds, so that the whole at the same time serves as a "sight."

Automatic Regulation of the Draught in the Chambers.—Especially in the case of chambers not connected with a high chimney, where changes of wind, etc., produce great variations of draught, it is advisable to adopt some automatic regulation together with the ordinary dampers, etc. Such an automatic apparatus can be made by putting on to the horizontal part of the exit-pipe a perpendicular 12-in. pipe, closed by a bell standing in an annular water-lute. The bell hangs on one arm of a lever, the other arm of which is so weighted that the bell can travel freely. When the draught is just right, this second arm has a certain position, in which a throttle-valve within the exit-pipe connected with it is half open. When the draught increases, the bell descends, owing to the increase of atmospheric pressure, and partly shuts the throttle-valve; in the opposite case of the draught decreasing, the throttle-valve is opened wider. This apparatus, as constructed by M. Delplace, is shown in Fig. 256, where *a* is the entrance-pipe from the Gay-Lussac tower, *c* the exit-pipe, *b* a conical valve, *d* the regulating bell, *e e* the water-line of the hydraulic joint, *f* the lever, *g* the balance-weight.

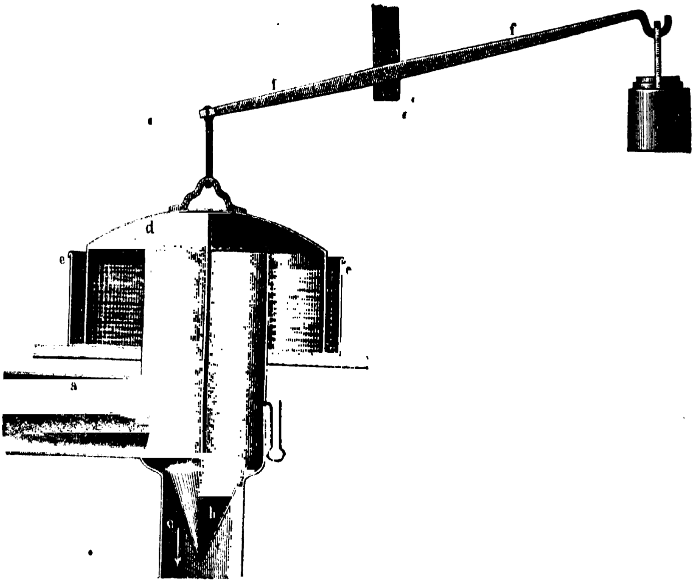

FIG. 256.

Somewhat different in detail, and apparently very accurately working, is the apparatus of Mr W. G. Strype, of Wicklow, of which the following is a description (B. P. 705 of 21st February 1879):—

The drawings illustrate two forms of the apparatus, Fig. 257 being the most desirable, although somewhat more expensive in construction than the arrangement shown in Fig. 258. Referring to Fig. 257, an inverted vessel or receiver A, open at its lower end, dips into a tank A′, containing water or other suitable liquid acting as a hydraulic joint. The interior of A is placed in communication, by means of the pipe or passage, *a b c*, with a receptacle R connected with the main flue from the Gay-Lussac towers and chambers. This receptacle is also in communication with a flue leading to the chimney, or other device for supporting the draught, and is divided by a partition having apertures fitted with valves or dampers, D D, made of an alloy of lead and antimony. The operation of opening and closing D D to ensure uniformity of draught is regulated automatically by the action of the suction itself in the following manner:—The dampers are connected to a lever B, mounted

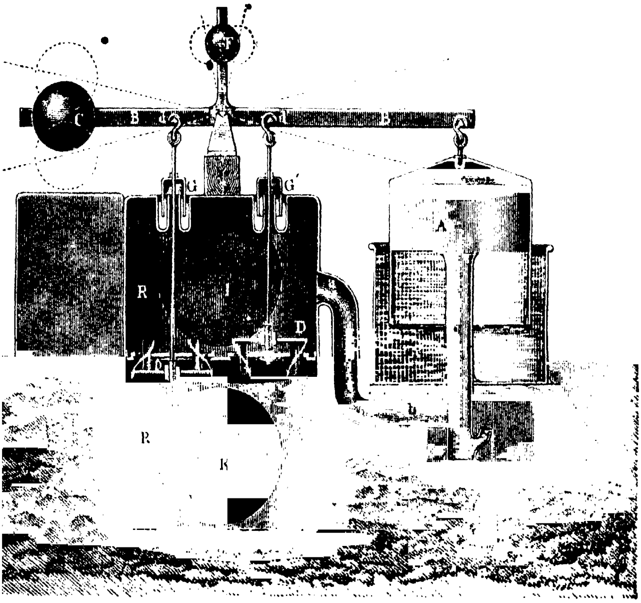

FIG. 257.

and turning on a centre or fulcrum *e*. Suspended from one end of the lever is the vessel A, whilst the opposite end is loaded with a weight G, sufficient to preponderate to the required extent over the load of A. Assuming that the draught has an excess of "pull" over that which is adjusted and necessary for the proper working of the chambers, the dampers being open, the suction within the vessel A, when accelerated, will draw down that end of the lever and elevate the opposite or weighted end, and so partially close the dampers. C is so calculated that the weighted end of the lever can only be elevated when the required draught is exceeded, and it will fall by gravitation as soon as the draught is unduly diminished. It follows that thus the desired uniform action is obtained.

The connection between the dampers and the lever B is by means of rods or links passing through water-sealed stuffing-boxes, G G′; and to avoid friction these rods are suspended from knife-edge centres, *d d′*. The other centres are constructed with knife-edges in like manner.

The vessel A becomes sensibly *lighter* when deeply immersed in the liquid, owing to the thickness of the sides, and would

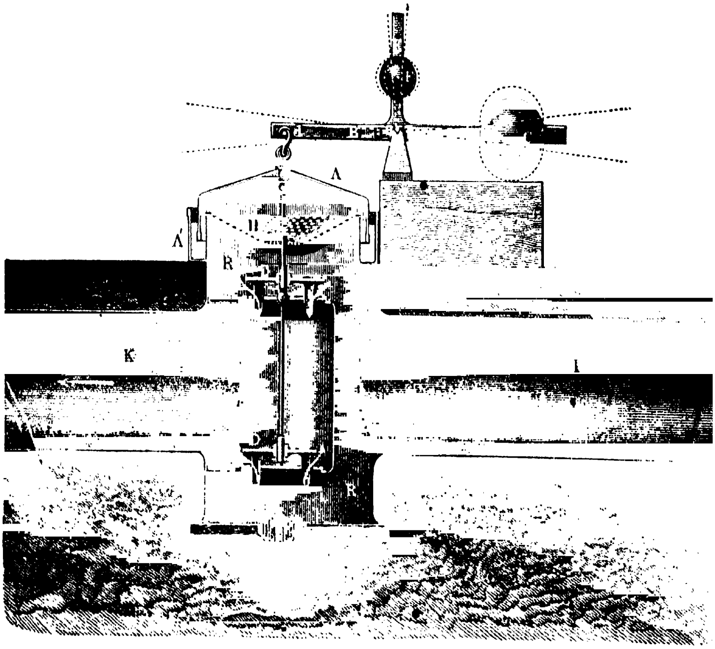

FIG. 258.

thereby constitute a source of disturbance to the proper action of the apparatus. To counteract this, the lever B is provided with a projecting arm E, carrying an adjustable weight F, arranged in such a position that, as the arm partakes of the motion of the lever, the centre of gravity of the system will be moved in the direction and to the extent necessary to effect the required correction.

Fig. 258 is a simpler, and in some applications a more convenient form of the apparatus, the action being of course identical with that described for the arrangement in Fig. 257. Should the draught fluctuate very much, the diaphragm shown dotted at H (with an opening in its centre to communicate with the vessel A) can be interposed to prevent the movements of the regulator being too sudden and rapid.

This apparatus has no wearing surfaces, is practically frictionless in its working, and is balanced in all positions. By means of it any disturbance to the steady and uniform flow of gases through the chambers caused by irregular chimney-draught is prevented, the admission of air to the burners is more uniform, the regulation of the proper quantity and relation of the gases to each other throughout the chambers is facilitated, and better working and more economical results are obtained in the process with less supervision and attention than hitherto required to carry on successfully the manufacture of sulphuric acid.

Mechanical Production of Draught by Fan-Blasts.

We have spoken above (p. 744) of the various drawbacks connected with the application of injectors for this object: I have indeed not found such apparatus at any of the works I have recently visited. But several works have adopted the plan, originally followed at Freiberg,[1] of promoting the draught by *fans* made of lead alloyed with antimony, or wood or iron covered with lead, fixed on iron axles, running in somewhat tightly fitting lead journals without stuffing-boxes. Such fans are arranged either between the Glover tower and the first chamber, or between the last chamber and the Gay-Lussac tower, or in both places. These fans are worked at a trifling expense, most conveniently by electro-motors, which avoid the necessity of shafting and gearing; and they should be more frequently employed, not merely in such extreme cases as at the Freiberg works, where the gases must travel through flues of 330 ft. length, but in connection with ordinary chambers, which are thus made independent of accidental variations of pressure, of low chimneys, etc.

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[1] According to Mühlhäuser (*Z. angew. Chem.*, 1902, p. 672), this invention is due to a mining engineer of the name of Hagen, at the Halsbrücke works.

At the works of Messrs Matthiesen and Hegeler at La Salle (Ill.), where zinc-blende is roasted in a mechanical shelf-burner, and the necessary draught for the chambers could not be obtained by a chimney, an iron fan-blast, covered with an alloy of lead and antimony, is placed between the Glover tower and the first chamber, and another such apparatus between the Gay-Lussac tower and the chimney. This arrangement had been working for several years when I visited the works in 1890.

The systematic production of draught by placing one fan behind the Glover tower and another in front of the Gay-Lussac has been especially worked out by F. J. Falding: cf. *Min. Ind.*, vii. p. 672. In this way the draught of the burners is rendered independent of the pressure in the chambers, where quite different conditions prevail.

Falding's fans have a cast-iron casing lined with lead, and a spindle and arms made of antimony-lead. They are very carefully and substantially mounted, and work up to 700 revolutions per minute.

Niedenführ (1902) considers that a fan-blast would be best placed between the burners and the Glover tower, but he believes this to be impossible with ordinary fans on account of the high temperature and the flue-dust. Directly behind the Glover tower a fan would also act very well, but here antimony-lead is too quickly corroded, and it is therefore generally preferred to put the fan between the last chamber and the Gay-Lussac tower. The firm of March Söhne, at Charlottenberg (now "Vereinigte Thonwaarenwerke"), have constructed very good fans of stoneware, which probably will do perfectly well at temperatures below 70° C., for instance, between the Glover tower and the first chamber (cf. *Chem. Zeit.*, 1902, p. 1057). But even in that case it is best to place another fan between the last chamber and the Gay-Lussac tower. In very long sets with small sections, such as are found when a small original plant is gradually enlarged by adding more chambers, there is frequently irregular work, with large consumption of nitre, which is very easily remedied by a rational use of fan-blasts.

Usually the fans are made of iron covered with lead, or altogether of "hard lead" or "regulus" (antimonial lead), but of course the axle or spindle should be made of iron, and the journals must also consist of this metal. This is a weak point, at least where there is heat to contend with as well as the acids. In very hot places, however, where lead is out of the question, cast-iron may be employed, which is not acted upon so long as no acid is condensed upon it. Here also the journals are the weak point, but this has been overcome by A. P. O'Brien, at Richmond, Va.; in the following manner (Falding, *Min. Ind.*, ix. p. 621):—A cast-iron fan is placed immediately behind the burners, before the nitre-oven and Glover tower. It serves five Herreshoff furnaces, consuming 30,000 lb. 49 per cent. Rio Tinto fines per twenty-four hours. The fan has 27 in. suction and discharge, and is made of cast-iron throughout, including the spindle: it is covered with a 1-in. coat of asbestos cement. The temperature inside the fan is about 540° C. The journals are not oiled at all, but flooded with water from several ⅜-in. pipes. Water also surrounds the jacket of each journal, and is admitted to the oil-chamber in lieu of oil as a lubricant. After nine months' work it had not required a cent's worth of repair or oil. No wrought-iron or steel is in contact with the gas, only cast-iron; otherwise there is nothing special in its construction.

Petschow (*Z. angew. Chem.*, 1903, p. 12) quotes some misadventures with fans made of stoneware. Plath (*ibid.*, p 159) and Niedenführ (p. 161) controvert his statements and prove the success of such fans. As built by the Vereinigte Thonwaarenwerke, of Charlottenburg, they perform a duty of 120 cb.m. or 4200 cub. ft. per minute. Petschow (*ibid.*, p. 304) practically yields the point. In 1905 (*Z. angew. Chem.*, 1905, p. 1264) Plath especially recommends a stoneware fan, called "Frithjof," built on a new plan by the Charlottenburg factory. In 1907 (*Z. angew. Chem.*, 1907, p. 444) he recommends placing stoneware fans of the ordinary type between the chambers and armoured fans of the Frithjof type in front of the first chamber, where they can stand temperatures of 100°.

Benker and Hartmann (*Z. angew. Chem.*, 1903, p. 861) place the fan where two Gay-Lussacs are provided, between these;

if there is only one Gay-Lussac tower, the fan is placed either between this and the last chamber, or else behind the Gay-Lussac, and in this case they prefer putting behind the fan a Lunge-Rohrmann plate-tower (p. 657) in order to condense the acid fumes which are always present in the gases, where only one Gay-Lussac tower is provided. The last gases escape straight into the outer air or into a chimney. They recommend P. Kestner's fan made of hard lead, which makes only from 300 to 700 revolutions per minute, requires from $\frac{1}{2}$ to 1 h.p. and aspirates from 1000 to 8000 cb.m. per hour; it is driven either by a small steam-engine or an electro-motor.

Kestner (*J. Soc. Chem. Ind.*, 1903, p. 333; more explicitly in *Verhandl. V. Kongress fur angew. Chem.*, 1905, i. pp. 623 *et seq.*) is also of opinion that the best place for a fan is behind the chambers. If placed between the burners and the Glover tower, its construction is rendered enormously difficult on account of the heat and the impurities of the burner-gases, and this is still the case where it is placed between the Glover and the first chamber. In both cases leaden fans are quickly corroded and stoneware fans are easily cracked. The advantage of increasing the pressure in the chambers by placing it before them is extremely slight, amounting only to about $\frac{1}{2000}$ of the atmospheric pressure. Kestner's fans, placed at the end of the chamber system, of which upwards of sixty were already at work at that time, possess a wheel made of antimony-lead ("hard lead") and a case of the same material or of Volvic lava; they rotate but slowly and are usually driven by a special steam or electric engine. The part played by the fan-blast is not to draw more air through the chambers, but to keep the current of air constant, not influenced by the variations of the atmospheric pressure, temperature, wind, sunlight, etc. According to *Chem. Zeit.*, 1910, p. 734, Kestner has increased the usefulness of his hard-lead fans by a special construction with back-suction for hot gases and high pressures.

Figs. 259 to 261 show a hard-lead fan as constructed by H. Leutpold, at the Dora-Lys works at Pont Saint-Martin (communicated by him to me). Fig. 259 is a sectional elevation, Fig. 260 a sectional plan, Fig. 261 a perspective view of the iron casing. It is clearly seen how the iron spindle is protected by a hard-lead casing.

Benker (1902) always employs fan-blasts (and water-sprays) for the "high-pressure work" (*cf.* pp. 659 *et seq.*, and Chapter VII.) where 8 kg. acid of 116° Tw. is made per cubic metre in twenty-four hours. He places the fans preferably between two Gay-Lussac towers; if there is only one Gay-Lussac, the fan is placed behind this, but is followed by a small tower fed with water in order to condense the acid mist. For this purpose Benker prefers Lunge's plate-towers to any other kind of apparatus; he places one of these towers at such a height

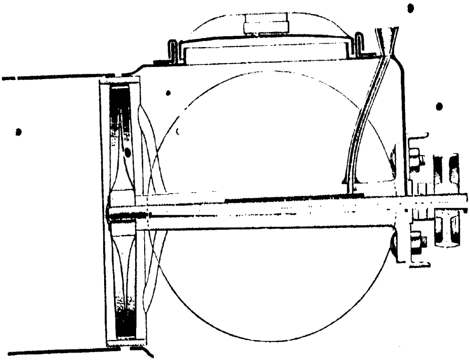

FIG. 259.

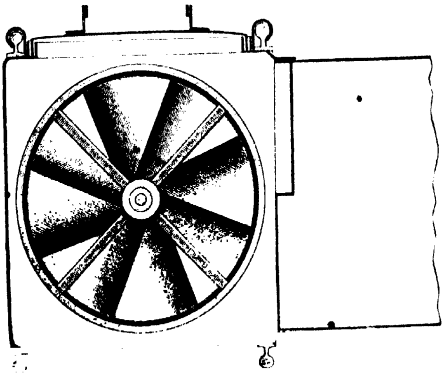

FIG. 260.

that the weak acid contained therein can be run into the Glover tower. The object of the fan-blast is to avoid the inequalities and temporary losses of draught caused in the case of chimneys by wind, sunshine, etc., and to produce a regular composition of the exit-gases, 4·5 to 5 per cent. oxygen for ordinary pyrites, up to 6·5 per cent. for cupreous pyrites. As there is a difference of temperature between day and night, the speed of the fan must be regulated at least twice a day. Benker states that attempts at placing a fan between the Glover tower and the first chamber were not successful principally on account of the necessity of frequent repairs, although even shells made of Volvic lava were tried.

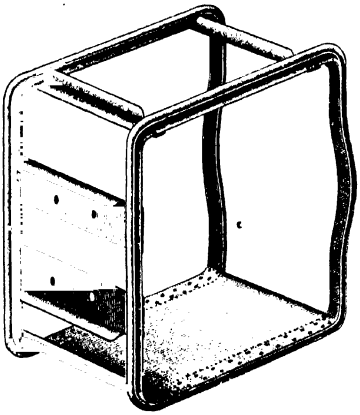

FIG. 261.

The question of employing fan-blasts for acid-chambers has received a new impetus by Niedenführ's Ger. P. 140825, which provides two Glover towers in succession, to fulfil separate functions, the fan-blast being placed between them. This question will be treated in the next chapter, when discussing the functions of the Glover tower.

Lüty (*Z. angew. Chem.*, 1905, pp. 1253 *et seq.*) greatly approves of the use of fans, especially in the way adopted by Niedenführ, but we shall see anon that this is strongly contested from other sides.

The Vereinigte Tonwarenwarke, Berlin, propose to place stoneware fans in the corners of lead chambers, with stoneware pipes penetrating through the side of the chambers, for protecting the shafting, in order to cause a strong whirl-movement in the chambers.

Rabe (*Z. angew. Chem.*, 1905, pp. 1735 *et seq.*) discusses at length the part which fan-blasts play in the lead-chamber process. This is merely the task of overcoming the friction in the single parts of the apparatus. It is not correct to speak of an "increase of draught," since behind the fan-blast as well the pressure is increased. It is merely an apparatus for moving the gases from one side to the other. The velocity of the gas on the side of aspiration is essentially the same as on the side of pressure, although the pressure is different on both sides. At a difference of pressure amounting to a water-column of 50 mm., which is quite an extreme case in the application of fan-blasts in the lead-chamber process, the difference of velocity between the gas entering and that leaving the fan is only 0·5 per cent. by volume, or half of it = 0·25 per cent. as against working with ordinary draught; and if, as is quite necessary in our case, not the volumes, but the weights are considered, even that slight difference vanishes entirely, and we may take the difference in the movement of the gases = zero. Hence it is quite indifferent for the movement of the gas in which place the fan-blast is put, whether in front of the burners (which has certain advantages), or in front of or behind the Glover, or at the Gay-Lussac, or anywhere else. It is impossible to influence the gas only on *one* side of the fan. But of course certain reasons exist for placing the fan in one or the other of those spots. If special regard is to be had to spending as little as possible on driving force, the fan is best placed at the end of the system, where the volume of the gas is lessened by 12 per cent. through the condensation of the sulphuric acid. If it is required to bring the fan into contact only with pure air, it must be placed in front of the burners, which in this case, of course, must be provided with a closed conduit of air. If the fan is sufficiently resistant to hot acid gases, it is placed in front of the Glover (Falding's system). If, however, it is to be in contact only with *cold* acid gases, these must be previously cooled, as is stated in the Ger. P. 140825, quoted *suprà*. The performance of the fan-blast in overcoming the friction in the various parts of the apparatus makes it possible, either to employ apparatus offering greater resistance to the current of gas, or to pass more gas through the chambers than can be done by natural draught. In the former case apparatus for precipitating the flue-dust, for utilising the heat, and generally for making the chamber process more rational may be interposed in already existing plant, without in any way diminishing the quantity of the gases. In the second case the velocity of the gaseous current may be altogether increased, since we are then not confined to the "natural" draught, and this means an increase of the production of the chambers. In these cases as well it is indifferent in which place the fan-blast is interposed, since in most descriptions of fans it is pretty immaterial whether the greater resistance takes place in the aspirating- or in the pressure-conduit.

The regulation of the work of the fan-blast is best performed in immediate connection with it, whether by changing the number of revolutions, or, where this is impossible, as in the case of working a rotating current, by throttling. In any case the aim should not be that of producing a certain plus- or minus-*pressure* against that of the atmosphere, but that of producing a certain *velocity* of the gases, as shown by instruments indicating this, since these are independent of any obstructions in the gas conduits, etc., and since it is important to work with gas of a uniform percentage of SO_2. Of course it is also desirable to observe the pressure in every part of the apparatus, as this admits of early recognising the constancy of the friction exerted. Thus the chamber work is more easily controlled, and the velocity of the gas current can be kept constant, as long as there is an excess of power in the fan-blast. Of course it is not permissible to work the fan-blast in such manner that the towers or chambers are damaged by an excess or a minus of pressure against that of the atmosphere. But Rabe has already succeeded in working for a long time with a plus-pressure equal to 180 mm. water, on large, not supported, surfaces of lead, without any damage being done. In the case of new plant it is best to effect from the outset the smallest possible friction in the apparatus and conduits, as fan-blasts work more economically with smaller differences of pressure. It has also been proved that for the intimate contact of gases and liquids, *e.g.* in reaction towers, not an increase of friction by overpressure in the towers, but exclusively an increase of the surface of contact between the gas and the liquid is of importance. Hence apparatus involving greater friction must be employed only where it is from any reasons whatever, cheaper than apparatus with smaller frictions, if the cost of working and of writing-off is calculated. When the fan-blast is worked more or less, both parts of the gas conduit, that in front and that in the rear, are influenced in the same way. Hence it is not possible to influence the roasting process differently from the chamber process, where the fan is placed between them ; nor is this possible where it is placed elsewhere, since these parts are always dependent upon each other. If the fan-blast is throttled, less air must enter into the burners, and they will eventually blow out, the gases becoming richer in SO_2. This acts upon the chamber precisely in the same way as any insufficiency of "draught" or of oxygen. In the opposite case, that of increasing the action of the fan, the roasting goes on more quickly, but the percentage of SO_2 is diminished and the chamber process disturbed. These drawbacks happen precisely in the same manner, whether the fan be placed between the burners and the chamber (Falding's plan), or between the concentrating- and denitrating-tower (Niedenführ's Ger. P. 140825, *suprà* p. 758), or in the rear of the chambers (Kestner's plan, p. 756). It is impossible to render the roasting and the chamber process independent of each other, but it is possible to make the work independent of the resistance by friction, whether this be permanent or produced within the course of working. Nor can the absolute pressure within the chambers be essentially altered; the places immediately in front and in the rear of the fan may show differences of, say, 50 mm. water pressure, but the remoter parts show much less, down to 0·025 per cent. of the atmospheric pressure, which is altogether insignificant in comparison with the differences of atmospheric pressure which may reach 2 per cent. The propulsion of the gases is precisely the same whether there is a plus- or minus-pressure, both in the Glover and in the chamber, other circumstances being equal. It is erroneous to assume that a plus-pressure by itself is essential for the movement of the gases; nor that such a pressure forces the gases to penetrate into every part of the apparatus and to avoid "dead corners." It is certainly true that the best utilisation of an apparatus to a great extent depends upon the way in which the gases travel therein, so that it is very important to find out the best conditions therefor; but it is quite unessential whether this work is done by plus- or by minus-pressure. The decisive moments are: the shape of the outlet openings of the conduits, the specific gravities of the gases produced by the reactions, and the place where they are introduced. In working with fan-blasts gyratory motions have been spoken of as taking place, but these occur precisely in the same way with plus- or with minus-pressure, and they cease in longer conduits. If the higher pressure by itself produced the assumed effects, the same differences would appear without fan-blasts between factories situated at a higher or lower level, and the daily oscillations of atmospheric pressure would influence the working of the chambers to an alarming extent. Every chamber manager knows that he must take regard of these; but his task is not that of increasing the plus- or minus-pressure, but to regulate the velocity of the gas so that the proportions of *weight* are kept constant. The plus- or minus-pressure has nothing to do with this; the reactions are essentially the same in both cases; neither is there a special movement of the gases, nor a more intimate contact of the molecules, and the alleged proofs for the contrary are not correct. This Rabe also applies to Lüty's paper in *Z. angew. Chem.*, 1905, pp. 1253 *et seq.*; the results adduced by him are much better explained by differences in the size of the apparatus, the still of work, the cooling action, etc., and they have nothing to do with the place given to the fan-blast.

Hüppner (*Z. angew. Chem.*, 1905, p. 2001) insists against Rabe that the work done by the fan is not in proportion to the weight, but to the volume of the gases, and that the way of measuring the pressure, recommended by Rabe, does not absolutely avoid the mistakes pointed out by him.

M. Neumann (*Z. angew. Chem.*, 1905, pp. 1814 *et seq.*) criticises the plan of Niedenführ (Ger. P. 140825, *vide* p. 758) and Lüty's remarks upon it (*ibid.*). A higher than the formerly usual pressure of 2 or 3 mm. water in the beginning of the first chamber, say 4 to 7 mm., has been first used in America, before the date of Niedenführ's patent. It is quite wrong to assume that such a slight increase of pressure can have any influence on the chamber process, as already pointed out by Benker and Hartmann (*suprà* p. 758; *cf.* also Rabe, p. 759). All the advantages claimed by Niedenführ and Lüty for that rise of pressure can be but very slight. Fan-blasts, made of cast-iron, lined with lead, the wheel being made of antimony-lead and mounted upon a lead-covered steel shaft, have been employed since 1894 between the Glover and the first chamber; Falding (*cf.* p. 755) and others have put up more than fifty of these, and in the United States there is hardly a sulphuric-acid factory working otherwise than with fan-blasts. Falding employs a second less powerful fan at the end of the system, and is thus able to make all parts of the system independent of each other. Recently Falding recommends O'Brien's fan (*suprà* p. 755), which is entirely made of cast-iron and is placed between the burners and the Glover in a place where it is too hot for acid to condense and to corrode the metal. The separation of the Glover into two towers, claimed by Niedenführ, is also an American invention, and already in 1894 Falding obtained the Ger. P. 76691 for it; also Zanner, Ger. P. 134661, who certainly does not entirely divide the two functions of the Glover on two towers, but effects only part of the concentration by a special apparatus interposed between the Glover and the first chamber. Plath's armoured stoneware fan, the "Frithjof" (*cf.* p. 755), can be easily put in that place. The "intense" production of acid in the chambers practised so much recently and also aimed at by Niedenführ and Lüty, must of necessity cause a much faster wear and tear of the chambers, so that the life of a chamber, instead of twenty to twenty-five years, will be only ten or twelve years. Thus, as Neumann asserts, nothing original and useful remains of Niedenführ's system, so much commended by Lüty.

Schliebs (*Z. angew. Chem.*, 1905, pp. 1900 *et seq.*) has had most favourable experience with fans placed between the Glover and the first chamber. He further advocates his view (*ibid.*, 1906, p. 571).

Niedenführ (*Z. angew. Chem.*, 1906, pp. 61 *et seq.*) replies to Rabe and to Neumann. The velocity of the gaseous current ought to be as uniform as possible, beginning with the burners; hence the resistances should be reduced as much as possible and not vary very much. This leads to placing the fan as nearly as possible behind the burners, where it can best act against the causes of changes in the composition and velocity of the gases. The same consideration leads to a throttling of the outlet from the Gay-Lussac tower, which best takes place behind a second fan, placed there. Most sulphuric-acid factories now work with fans, and the author has always found the best results being obtained where the fan was placed in front of the first chamber, not in the rear part of the system; the latter position easily leads to an unhealthy forcing of the work. This conclusion, identical with the ideas of Falding (*suprà* p. 755), has been verified by experiences made with tangential chambers (p. 622) without his own concurrence, and has led up to a production of 12 kg. and of 1·53 sp. gr. per cubic metre—the highest ever heard of; even with rectangular chambers as much as 11·5 kg. have been realised. The author has up to now had to build 28 sets of chambers, and always made the same experience. Niedenführ then contradicts Rabe's assertion concerning the pressure under which the chambers should work, viz., that it is indifferent whether it is a plus-pressure or not. He quotes an instance of factories erected at great heights, *e.g.* one in Mexico at an elevation of 7000 ft. above sea-level, where the production of the chambers per cubic space is distinctly smaller than at lower levels. His best results were obtained when keeping in the chambers a pressure of from 4 to 8 mm. above that of the atmosphere; only then there are no places in them where the gases stagnate.—It is also very important to keep the temperature in the chambers at its most favourable height. For this reason in the "high-pressure" work the chambers are worked, not with steam, but with liquid water in the form of a spray, which is of the greatest advantage in chambers of considerable height; also to denitrate the gases at not too high a temperature, which is best done by dividing the functions of the Glover upon two towers (Chap. VI.). Neumann's opinion that this division causes a deficiency in the concentrating action of the Glover is refuted by experience, as well as his assertion concerning the great wear and tear of "intensely" working chambers.

Neumann replies to the above in the same journal, 1906, pp. 474 *et seq.*, at great length, but without bringing in any new matter.

Hartmann and Benker (*Z. angew. Chem.*, 1906, pp. 132 to 137) criticise a number of the statements and opinions pronounced by the preceding authors, and again insist on placing the fan at the end of the system, between the two Gay-Lussacs, or, if there is only one such tower, between it and the last chamber. They consider it wrong to place it in front of the Glover, except in the case of mechanical burners, where this is just the right place for a fan; but then they put a second fan at the end of the system (like Falding). In the case of ordinary burners for lumps or smalls the upward draught of the gases is sufficient by itself to send them into the chambers; if increased by a fan, placed between the burners and the first chamber, the pressure is too great and the life of the chamber is greatly shortened, and too much flue-dust gets into the Glover or even into the chamber. If the fan is placed at the end of the system, in front of the last Gay-Lussac, the gases enter it cold and dry, so that the fan is not damaged by them; it can be mounted below the tower and without stopping the work, and is later on easily accessible for repairs. In this place it is most efficient for overcoming the frictional resistance of the Gay-Lussac tower, as well as the difficulties caused by changes of the atmospheric conditions. They had at that time already provided about 150 sets of chambers with fans in that position, in works of all sizes, and situate in all industrial countries.

Th. Meyer (*ibid.*, pp. 523 to 525) defends his "tangential system" and the necessity of placing the fan *in front* of the tangential chamber, behind the Glover.

Hartmann and Benker (*ibid.*, pp. 953 to 956) assert that a plant erected at Roubaix according to Niedenführ's Ger. P. 140825 (cf. *suprà* p. 758) had given great dissatisfaction and had been dismounted after eight months' work; thereupon the plant was altered in Hartmann and Benker's plan, and now produced 12 kg. acid of 53° Bé. in twenty-four hours. The division of the Glover functions upon two towers did not answer, and the application of higher pressure did not answer.

The 42*nd Report on Alkali Works* (for the year 1905), p. 16, states that, concerning the use of mechanical means for creating the draught in acid-chambers, nothing but good has been said by those manufacturers who have adopted it, when once the necessary experience has been gained. The advantages of better control are recognised both by the manufacturer and the inspector. Local escapes from the burners certainly can be more readily avoided.

Processes for special modes of introducing the gases into the vitriol-chambers will be mentioned later on, *e.g.* Rabe's Ger. P. 237561, for aiding their movement according to Abraham's "spiral" theory.

Feigensohn (*Chem. Zeit.*, 1906, pp. 851 to 853) contradicts the assertions of Raschig concerning the "intense" production of acid in the chambers in *Z. angew. Chem.*, 1905, pp. 1281 *et seq.* (*suprà* p. 689). According to him the augmentation of the production of acid in a given volume of chamber space by means of increasing the circulation of nitrous compounds is not consequent upon the rise of temperature; but this increase is necessary in order to stand the manifold larger amount of gases passing through, and to allow any gases from leaving the chambers without being subjected to the catalysing action of the nitrogen compounds. According to his trials, there is more loss of nitre when placing the fan nearer the first part of the system than further on, and the increase of production of sulphuric acid per unit of chamber space does not make up for the greater loss of nitre. The best place of the fan is between two Gay-Lussac towers; in case of employing three such towers, between the second and the third, and when employing final Lunge towers, in front of these. The working of the chambers is then easy; the loss of nitre per 100 parts of chamber-acid produced is 0·4 to 0·6 parts of HNO_3 36° Bé. for pyrites, or 0·75 to 0·8 parts for blende and poor copper ores. When working the chambers at higher pressure, there is more sulphuric acid produced in the same chamber space, but the loss of nitre is greater. The total acidity of the exit-gases increases with higher or lower pressure in the first Gay-Lussac, and decreases when keeping the pressures alike. The sets working according to Lunge yielded exit-gases with the least amount of acidity.

Anemometers.

Although we have in a previous chapter (p. 451) warned against the use of a Combes' anemometer for regulating the access of air to the burners, because it is too delicate an instrument, and because it only shows the draught in the place which it occupies, we have here to speak of an anemometer better adapted for controlling the draught in vitriol-chambers. This is Péclet's *differential anemometer* as modified by Fletcher and Swan. Fletcher's modification is described in the *Third Annual Report on the Alkali Act*, 1863, by the Inspector, for 1866, pp. 54 *et seq.*; Swan's in the *Transactions of the Newcastle Chemical Society*, 26th January 1871. Péclet's anemometer is founded upon the physical principle that a current of air passing the open end of a tube causes a partial vacuum in the tube. If, therefore, a straight tube is introduced through a hole into a chimney, or into the draught-pipe taking away the chamber-gas, so that the gaseous current passes the open end of the tube at a right angle, a partial vacuum will be formed in the latter, proportionally to the velocity of the current; but the aspirating action of the chimney will be equally communicated to this tube. We must here distinguish between these two actions. To do this, we must introduce two tubes into the chimney, one of which ends straight, whilst the other is bent to a right angle, so that the current of air blows into it. Both tubes will now be affected by the aspirating action of the chimney; but in the straight tube this is *increased* by the aspirating action of the current crossing its open end, whilst in the bent tube it is diminished by the air blowing into it. The difference between the aspirating action of the two tubes is thus reducible to the action of the current of air; and by measuring it the speed of that current can be ascertained. For this purpose the two tubes are connected with a U-shaped glass tube containing water or another liquid; this will rise in one of the limbs to an extent corresponding to the difference of suction. Since the sucking-action of the chimney acts upon both limbs, it is eliminated, and the difference of level corresponds merely to the different action exerted by the current of air upon the straight tube, which it crosses, and the bent one, into which it blows. This action rises and falls with the speed of the current; and the latter accordingly can be deduced from it. Water (used by Péclet), on account of the friction exercised in the U-tube, is only adapted for currents of a greater speed than 5 ft. per second. Fletcher overcame this difficulty thus:—In order to lessen the friction, he employed two cylinders, *a a′* (Fig. 262), of 4 in. diameter, connected at the bottom by a narrow tube, *b*. This arrangement is ten times as sensitive as a U-tube of 0·4 in. width would be, since the area upon which the pressure acts is increased 100-fold, but the circumference upon which friction acts only 10-fold. The rising and falling of the liquid is observed by means of metal floats, *c c*, upon which a very fine horizontal line is marked by a lathe; and the scale, *d*, provided with a vernier and a very fine adjusting-screw, permits the difference of level, down to $\frac{1}{1000}$ part of an inch, to be read off. This is possible, not with water, whose mobility, owing to its adhesion to the glass, is too slight, but with *ether*, whose adhesion is only $\frac{1}{2000}$ of that of water. The two glass tubes, *e* and *f*, are inserted into the draught-pipe, *k*, by means of a cork, *g*, at right angles to the current of gas (so that it blows into the bent tube, *f*), and are connected by elastic tubes, *hi*, with *a a′*.

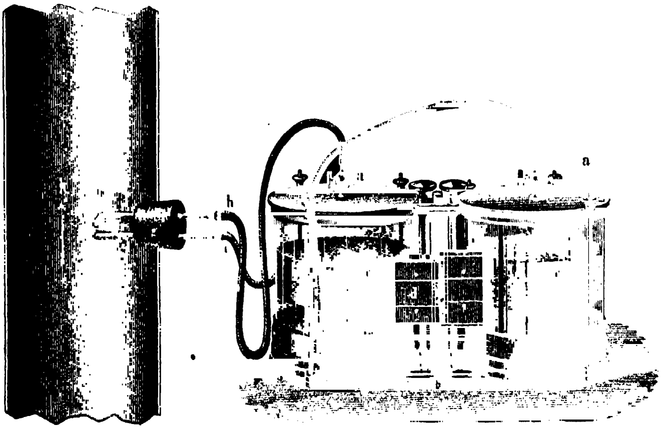

FIG. 262.

The form of anemometer shown in Fig. 262 has been simplified by myself, as shown in our last edition, p. 504, Fig. 244. We omit this here, as we shall lower down have to describe various new forms of anemometers.

In the original communication by Mr Fletcher, as well as in the first edition of this work (pp. 333 to 335), we find the mathematical evolution of the laws for ascertaining the relation of the readings to the speed of the currents. We abstain from repeating this reasoning here, and merely give the final formula found for ascertaining the velocity of the gaseous current v from the height of the column of ether (of 0·740 sp. gr.) $= p$, for any temperature t (in degrees Fahrenheit) and barometric pressure h (in inches):—

$$v = \sqrt{p \frac{29.92}{h} \times \frac{519}{459+t}} \times 28.55.$$

The table given on pp. 771 *et seq.*, for the speeds corresponding to different readings of the anemometer, is computed from the formula

$$v = \sqrt{p} \times 28.55;$$

and another table is added for correcting the variations in the temperature of the current of gas. The corrections for small variations in the barometrical pressure are usually not considerable; but they can be made by means of the above formula—

$$v'' = \sqrt{p \frac{29.92}{h}} \times 28.55,$$

or

$$v = \sqrt{p \frac{h}{29.92}} \times 28.55.$$

If the pressure is read off in millimetres the number 760 is everywhere substituted for 29·92; or if the readings are in millimetres and the speed in metres per second is required to be known, the constant 28·55 is converted into another, according to the formula

$$\frac{0.3048}{\sqrt{25.4}} \times 28.55 = 1.727;$$

so that the formula for v' and p' in metrical measures will read $v' = 1{\cdot}727 \sqrt{p'}$.

A correction for the expansion and contraction of the ether in the instrument itself is mostly unnecessary, since it is only exposed to the ordinary temperature; it amounts to about 1 per cent. of the speeds shown in the table for each 10° F. (=5·55° C.) deviation from 60° F.—more for temperatures below, less for temperatures above 60° F.

In order to make the readings more exact, first the height of ether in one of the limbs is noticed, then the current is reversed by connecting the tube *e* with *a* and *f* with *a′* (Fig. 262); another reading is made; and thus twice the difference of pressure caused by the suction at *f* is found. The number thus found is read off in Table I. and corrected for temperature by Table II. To take an instance, let the first reading be 1·039, and the second reading, after reversing the current, 0·861, the difference will be 0·178. On referring to Table I., the speed 12·05 ft. per second will be found. This, however, is only true if the temperature of the air is 60° F. Should it in the case in question be 520° F., Table II. gives the correcting multiplier, 0·7280. This, multiplied by 12·05, is 8·772, the true speed of the current if measured at the temperature of 60° F.

This instrument is not influenced by soot, heat, or corrosive vapours; it can be placed at some distance from the flue to be tested, if longer elastic tubing be used; and it can, of course, be employed both for aspirating and for pressure currents (fan-blasts, etc.), and as a measure for the speed of atmospheric currents.

Of course, like every other anemometer, Fletcher's only indicates the pressure at the place occupied by its receiving portion; and accordingly the tubes *e* and *f* must be introduced so far as to reach into the air-current to the extent of about one-sixth of the diameter of the flue. The velocity at this place is assumed to be nearly equal to the average; but this is very doubtful, and there are no means at present known of measuring the absolute quantities of air passing through a flue of any considerable sectional area with any degree of certainty.

TABLE I.—*Showing the Speed of Currents of Air as indicated by the Ether Anemometer.*

$$v = \sqrt{p} \times 28.55.$$

Temperature 60° Fahr. Barometer 29·29 in.

Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec	in.	ft. per sec.
0·001	0·903	0·047	6·189	0·093	8·707
0·002	1·277	0·048	6·255	0·094	8·754
0·003	1·564	0·049	6·320	0·095	8·800
0·004	1·806	0·050	6·384	0·096	8·846
0·005	2·019	0·051	6·448	0·097	8·892
0·006	2·212	0·052	6·510	0·098	8·938
0·007	2·389	0·053	6·572	0·099	8·983
0·008	2·554	0·054	6·634	0·100	9·028
0·009	2·709	0·055	6·695	0·102	9·118
0·010	2·855	0·056	6·756	0·104	9·207
0·011	2·994	0·057	6·816	0·106	9·295
0·012	3·127	0·058	6·876	0·108	9·383
0·013	3·255	0·059	6·935	0·110	9·469
0·014	3·378	0·060	6·993	0·112	9·554
0·015	3·497	0·061	7·051	0·114	9·639
0·016	3·612	0·062	7·109	0·116	9·724
0·017	3·723	0·063	7·166	0·118	9·808
0·018	3·830	0·064	7·223	0·120	9·891
0·019	3·935	0·065	7·279	0·122	9·972
0·020	4·038	0·066	7·335	0·124	10·053
0·021	4·137	0·067	7·390	0·126	10·13
0·022	4·235	0·068	7·445	0·128	10·21
0·023	4·330	0·069	7·500	0·130	10·29
0·024	4·423	0·070	7·554	0·132	10·37
0·025	4·514	0·071	7·608	0·134	10·45
0·026	4·604	0·072	7·661	0·136	10·53
0·027	4·691	0·073	7·713	0·138	10·60
0·028	4·777	0·074	7·766	0·140	10·68
0·029	4·862	0·075	7·819	0·142	10·76
0·030	4·945	0·076	7·871	0·144	10·83
0·031	5·027	0·077	7·922	0·146	10·91
0·032	5·107	0·078	7·974	0·148	10·98
0·033	5·187	0·079	8·025	0·150	11·06
0·034	5·265	0·080	8·075	0·152	11·13
0·035	5·342	0·081	8·125	0·154	11·20
0·036	5·418	0·082	8·175	0·156	[illegible]
0·037	5·492	0·083	8·225	0·158	11·34
0·038	5·565	0·084	8·275	0·160	11·42
0·039	5·638	0·085	8·324	0·162	11·49
0·040	5·710	0·086	8·373	0·164	11·56
0·041	5·781	0·087	8·421	0·166	11·63
0·042	5·851	0·088	8·469	0·168	11·70
0·043	5·921	0·089	8·517	0·170	11·77
0·044	5·989	0·090	8·565	0·172	11·84
0·045	6·056	0·091	8·613	0·174	11·91
0·046	6·123	0·092	8·660	0·176	11·98

TABLE I. (*continued*).

Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·178	12·05	0·284	15·23	0·390	17·83
0·180	12·11	0·286	15·28	0·392	17·88
0·182	12·18	0·288	15·33	0·394	17·93
0·184	12·25	0·290	15·38	0·396	17·98
0·186	12·31	0·292	15·44	0·398	18·02
0·188	12·38	0·294	15·49	0·400	18·06
0·190	12·45	0·296	15·54	0·402	18·11
0·192	12·51	0·298	15·59	0·404	18·16
0·194	12·57	0·300	15·64	0·406	18·20
0·196	12·64	0·302	15·70	0·408	18·24
0·198	12·71	0·304	15·75	0·410	18·28
0·200	12·77	0·306	15·80	0·412	18·33
0·202	12·83	0·308	15·85	0·414	18·38
0·204	12·90	0·310	15·90	0·416	18·42
0·206	12·96	0·312	15·95	0·418	18·46
0·208	13·02	0·314	16·00	0·420	18·50
0·210	13·08	0·316	16·05	0·422	18·55
0·212	13·15	0·318	16·10	0·424	18·60
0·214	13·21	0·320	16·15	0·426	18·64
0·216	13·27	0·322	16·20	0·428	18·68
0·218	13·33	0·324	16·25	0·430	18·72
0·220	13·39	0·326	16·30	0·432	18·77
0·222	13·45	0·328	16·35	0·434	18·82
0·224	13·51	0·330	16·40	0·436	18·86
0·226	13·57	0·332	16·45	0·438	18·90
0·228	13·63	0·334	16·50	0·440	18·94
0·230	13·70	0·336	16·55	0·442	18·99
0·232	13·76	0·338	16·60	0·444	19·03
0·234	13·82	0·340	16·65	0·446	19·07
0·236	13·88	0·342	16·70	0·448	19·11
0·238	13·94	0·344	16·75	0·450	19·15
0·240	13·99	0·346	16·80	0·452	19·20
0·242	14·05	0·348	16·85	0·454	19·24
0·244	14·11	0·350	16·89	0·456	19·28
0·246	14·17	0·352	16·94	0·458	19·32
0·248	14·23	0·354	16·99	0·460	19·36
0·250	14·28	0·356	17·04	0·462	19·41
0·252	14·34	0·358	17·09	0·464	19·45
0·254	14·40	0·360	17·13	0·466	19·49
0·256	14·45	0·362	17·18	0·468	19·53
0·258	14·50	0·364	17·23	0·470	19·57
0·260	14·56	0·366	17·28	0·472	19·62
0·262	14·62	0·368	17·33	0·474	19·66
0·264	14·68	0·370	17·37	0·476	19·70
0·266	14·74	0·372	17·42	0·478	19·74
0·268	14·79	0·374	17·47	0·480	19·78
0·270	14·84	0·376	17·52	0·482	19·82
0·272	14·90	0·378	17·56	0·484	19·86
0·274	14·96	0·380	17·60	0·486	19·90
0·276	15·01	0·382	17·65	0·488	19·94
0·278	15·06	0·384	17·70	0·490	19·98
0·280	15·11	0·386	17·75	0·492	20·02
0·282	15·17	0·388	17·79	0·494	20·06

TABLE I. (*continued*).

Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.	Anemometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·496	20·10	0·590	21·94	0·700	23·89
0·498	20·14	0·600	22·12	0·750	24·73
0·500	20·18	0·610	22·30	0·800	25·54
0·510	20·38	0·620	22·48	0·850	26·32
0·520	20·58	0·630	22·66	0·900	27·08
0·530	20·78	0·640	22·84	0·950	27·83
0·540	20·98	0·650	23·02	1·000	28·55
0·550	21·17	0·660	23·20	1·250	31·93
0·560	21·37	0·670	23·38	1·500	34·97
0·570	21·56	0·680	23·55	1·750	37·77
0·580	21·75	0·690	23·72	2·000	40·37

TABLE II.—*Showing the Values of* $\sqrt{\frac{519}{459+t}}$ *for Values of t from* 0 *to* 1000; *or Corrections for Temperature.*

t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	*t*, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	*t*, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
0	1·0634	130	0·9388	260	0·8497
5	1·0577	135	0·9348	265	0·8467
10	1·0520	140	0·9309	270	0·8438
15	1·0464	145	0·9270	275	0·8409
20	1·0409	150	0·9232	280	0·8380
25	1·0355	155	0·9194	285	0·8352
30	1·0302	160	0·9156	290	0·8324
35	1·0250	165	0·9119	295	0·8296
40	1·0198	170	0·9083	300	0·8269
45	1·0148	175	0·9047	305	0·8242
50	1·0098	180	0·9012	310	0·8215
55	1·0049	185	0·8977	315	0·8189
60	1·0000	190	0·8943	320	0·8163
65	0·9952	195	0·8909	325	0·8137
70	0·9905	200	0·8875	330	0·8111
75	0·9858	205	0·8841	335	0·8085
80	0·9812	210	0·8808	340	0·8060
85	0·9767	215	0·8775	345	0·8035
90	0·9723	220	0·8743	350	0·8010
95	0·9679	225	0·8711	355	0·7985
100	0·9636	230	0·8680	360	0·7960
105	0·9593	235	0·8649	365	0·7936
110	0·9551	240	0·8618	370	0·7912
115	0·9509	245	0·8587	375	0·7888
120	0·9468	250	0·8557	380	0·7865
125	0·9428	255	0·8527	385	0·7842

TABLE II. (*continued*).

t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
390	0·7819	595	0·7017	800	0·6420
395	0·7786	600	0·7000	805	0·6407
400	0·7763	605	0·6983	810	0·6395
405	0·7741	610	0·6967	815	0·6382
410	0·7729	615	0·6951	820	0·6369
415	0·7707	620	0·6935	825	0·6357
420	0·7685	625	0·6919	830	0·6345
425	0·7663	630	0·6903	835	0·6333
430	0·7641	635	0·6887	840	0·6321
435	0·7619	640	0·6871	845	0·6309
440	0·7598	645	0·6856	850	0·6297
445	0·7577	650	0·6841	855	0·6285
450	0·7556	655	0·6826	860	0·6273
455	0·7535	660	0·6811	865	0·6261
460	0·7514	665	0·6796	870	0·6249
465	0·7494	670	0·6781	875	0·6237
470	0·7474	675	0·6766	880	0·6225
475	0·7454	680	0·6751	885	0·6214
480	0·7434	685	0·6736	890	0·6203
485	0·7414	690	0·6721	895	0·6192
490	0·7394	695	0·6706	900	0·6181
495	0·7375	700	0·6691	905	0·6169
500	0·7356	705	0·6676	910	0·6158
505	0·7337	710	0·6662	915	0·6147
510	0·7318	715	0·6648	920	0·6136
515	0·7299	720	0·6634	925	0·6125
520	0·7280	725	0·6620	930	0·6114
525	0·7261	730	0·6606	935	0·6103
530	0·7243	735	0·6592	940	0·6092
535	0·7225	740	0·6578	945	0·6081
540	0·7207	745	0·6565	950	0·6070
545	0·7189	750	0·6552	955	0·6059
550	0·7171	755	0·6538	960	0·6048
555	0·7153	760	0·6524	965	0·6037
560	0·7137	765	0·6511	970	0·6026
565	0·7119	770	0·6498	975	0·6015
570	0·7102	775	0·6485	980	0·6004
575	0·7085	780	0·6472	985	0·5994
580	0·7068	785	0·6459	990	0·5984
585	0·7051	790	0·6446	995	0·5974
590	0·7034	795	0·6433	1000	0·5964

Fletcher's anemometer has been improved by Swan in the following way, practically returning to Péclet's original construction (a similar plan has been independently proposed by P. Hart, *Chem. News*, xxi. p. 200). In lieu of the 4-in. cylinders he takes a U-tube of ⅛ in. diameter, narrowed in the bend to diminish the oscillations. The tube is 10 in. long, and placed with an inclination of 1 : 10; each limb has a scale and vernier, the latter partly made of glass and covering at the same time the scale and the tube, so that it is easy to read off to $\frac{1}{100}$ in. The ends of the tube are connected with a two-way cock, so that the current can be reversed without opening any joint. Fig. 263 shows the instrument as seen from above, so that its inclination to the vertical line does not appear. It is fixed on a stand provided with a spirit-level and adjusting-screws. It is employed just like Fletcher's anemometer; but, owing to the inclination of 1 : 10, the column of ether in the tube occupies ten times the space corresponding to its height, and the reading of $\frac{1}{100}$ in. gives thus the same result as the very difficult one to $\frac{1}{1000}$ in. in Fletcher's instrument. The narrowness of the tubes does not matter in the case of ether, as the friction may be entirely neglected with this substance (the later form of Fletcher's anemometer, shown in Fig. 262, bears this out as well). Swan's anemometer must always be placed exactly level in the direction of its length; but it need not be levelled across, if a reading be made in one limb, the two-way cock turned, and the new reading in the same limb subtracted from the first; thus it is unnecessary to read off at both limbs, which would involve levelling across as well. The speeds are found from Fletcher's table, dividing the readings by 10.

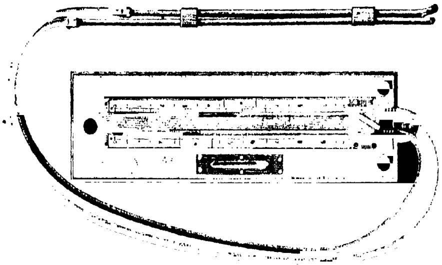

FIG. 263.

Other instruments for measuring the draught are, for instance, those of Kretz (*Dingl. polyt. J.*, cxc. p. 16), of Ramsbottom (*ibid.*, clxxx. p. 334), of Scheurer-Kestner (*ibid.*, ccvi. p. 448, and ccxxi. p. 427), none of which can vie with Fletcher's in sensitiveness. The very ingenious anemometer of Hurter (*ibid.*, ccxxix. p. 160) is only adapted for laboratory use. *Cf* also Bourdon's multiplying anemometer (*Comptes rend.*, xciv. p. 5; *J. Soc. Chem. Ind.*, 1882, p. 60).

One of the most delicate anemometers is Fryer's, described in the *Inspector's Report on the Alkali Acts for* 1877-1878, p. 68. Its principle is to measure the difference of pressure on each side of a watch-glass shaped copper plate connected with a spiral spring. It will measure a pressure of $\frac{1}{3000}$ of an inch.

Recently differential anemometers on another principle have come into use very largely, and seem to be preferable to all others. There are already a good many forms of this apparatus, one of the best known being that of Professor Seger (Ger. P. 19426), shown in Fig. 264. The calibrated U-tube A is surmounted by two cylindrical cups, B and C, of equal width. The board on which it is fastened also carries the sliding-scale D, adjustable by slits *a a* and screw-pins, *b b*. The tube is filled with two not miscible liquids, for instance heavy paraffin oil and dilute, coloured spirits of wine, of nearly equal specific gravity, to such an extent that the zero-point of the scale D can be put exactly at the line of contact of both liquids at X. If an aspirating force is acting on the surface of the liquid in C, which raises the level in that part of the tube, the point X will be lowered at a multiplied ratio, corresponding to the difference in the sectional area of the narrow part of A and the enlargement in C. If, for instance, the ratio of the sections is as 1 : 20, a difference of pressure of 1 mm. will be indicated on the scale by a sinking of X to the amount of 20 mm. The scale is graduated in such a way that it indicates the pressure expressed in millimetres of water.

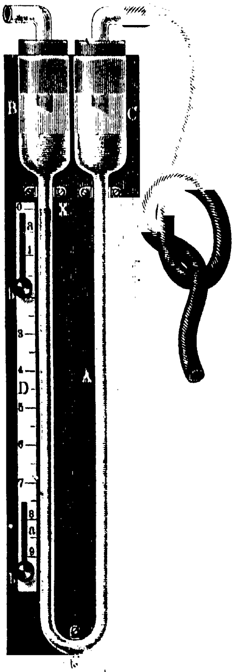

FIG. 264.

This instrument is much cheaper and easier to handle than those constructed on Péclet's principle and quite as accurate.

A very sensitive *pressure-gauge* has been described by Vogt (*J. prakt. Chem.*, xiv. p. 284). The pressure is observed by the movement of a small air-bubble playing in a horizontal glass tube of 4 or 5 mm. diameter. The glass tube, besides this bubble, is filled with water or another liquid, and is connected on each side with a bottle tubulated near the bottom. One of these bottles is 15 to 16 c.c., the other 6 to 8 c.c. wide; the liquid stands at the same level in each. The pressure within the lead chamber is made to act upon the surface of the liquid in one of the bottles, and its amount measured by the position of the air-bubble. The apparatus is all the more sensitive the greater the difference between the diameter of the tube and that of the bottles. There is a contrivance for admitting a bubble of air previous to using the apparatus, and for again equalising the levels after use.

A very simple pressure-gauge, sufficiently sensitive for ordinary purposes, is shown in Fig. 265 (from Sorel, *Industries*

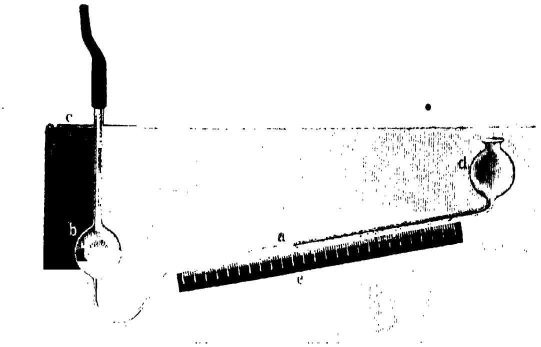

FIG. 265.

Chimiques, p. 142). The tube *a* has an inclination from the level in the proportion of 1 : 10; it is connected with a reservoir *b*, 1½ or 2 in. wide, upon which the pressure is brought to act by the elastic tube *c* (if there is suction, the vessel to be tested must be connected with the bulb *d*). The gauge is filled with a mixture of water and spirit of wine coloured with magenta or otherwise. As the movement of the liquid in the bulb *b* can be neglected, any movement of the liquid in the tube *a*, as measured on the scale *e*, corresponds to one-tenth of its extent in real height. If, for instance, each degree on the scale is $=\frac{1}{10}$ in., it indicates a real pressure of $\frac{1}{100}$ in. It is best to cause the liquid to move before each observation, in order to counteract the effect of friction within the tube.

The measurement of the velocity of a current of gas can be carried out by measuring the pressures before and behind a throttling arrangement interposed in the conduit-pipe. On this principle is constructed the instrument of Dr H. Rabe (Ger. P. 111019), described in *Z. angew. Chem.*, 1900, p. 236; 1901, p. 950; 1903, p. 136.

General Remarks on the Measurement of the Draught.

Rabe (*Z. angew. Chem.*, 1905, p. 1735) draws attention to erroneous ideas frequently entertained on the indications given by pressure-gauges and anemometers. It is a mistake to assume that the velocity of a gaseous current can be directly inferred from the indication of the pressure-gauge. They merely show the difference of pressure between the apparatus to which they are attached and the outer air. It is different with "anemometers" like those described above, where *both* limbs of the instrument shaped in a special way are introduced into the apparatus, whereas in ordinary pressure-gauges only one of the limbs is connected with the apparatus to be tested. By "velocity of the current of gas" we must understand the proportion of the quantity of the gas to the unit of time which the gas takes to pass through a unit of space in the apparatus, *e.g.*, if 10 cb.m. of the gas pass through 1 cb.m. of the apparatus in one second, we speak of a gas-velocity = 10; indifferently, whether the conduits are wide or narrow, and whether the apparatus is empty or filled with packing, since only the space really occupied by the gas is taken into consideration. Nor does any throttling change the proportional velocity of the gas in the parts in front or behind, since the movement takes place on both sides of the throttling-valve. Hence it is indifferent in which part of the chamber system the throttling takes place, whether before the air enters the burners, or where the gases

Percentage of H_2SO_4 in the acid.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.	85°.	90°.	95°.
44	1·042	1·063	1·085	1·108	1·133	1·160	1·192	1·225	1·263									
46	1·042	1·062	1·084	1·107	1·131	1·157	1·188	1·218	1·256	1·303	1·356	1·427						
48	1·042	1·062	1·083	1·105	1·129	1·155	1·185	1·212	1·249	1·292	1·341	1·397	1·478	1·542				
50	1·041	1·061	1·082	1·104	1·128	1·152	1·180	1·207	1·241	1·281	1·327	1·377	1·45[illegible]	1·509	1·589	1·756	1·911	
52	1·041	1·060	1·081	1·103	1·125	1·150	1·177	1·202	1·234	1·270	1·313	1·359	1·429	1·478	1·562	1·662	1·830	2·014
54	1·040	1·060	1·080	1·102	1·122	1·147	1·175	1·198	1·227	1·260	1·301	1·343	1·408	1·419	1·526	1·625	1·752	1·904
56	1·040	1·059	1·079	1·100	1·121	1·144	1·169	1·194	1·222	1·252	1·290	1·328	1·388	1·423	1·490	1·589	1·684	1·813
58	1·039	1·059	1·078	1·099	1·120	1·142	1·166	1·190	1·215	1·244	1·279	1·313	1·369	1·400	1·456	1·534	1·625	1·734
60	1·039	1·058	1·077	1·098	1·119	1·140	1·163	1·186	1·209	1·237	1·269	1·299	1·352	1·368	1·428	1·495	1·575	1·668
62	1·038	1·058	1·077	1·097	1·118	1·138	1·160	1·182	1·204	1·230	1·261	1·289	1·335	1·357	1·402	1·462	1·532	1·613
64	1·038	1·057	1·076	1·096	1·117	1·136	1·158	1·178	1·200	1·224	1·253	1·279	1·322	1·337	1·379	1·431	1·493	1·562
66	1·038	1·057	1·076	1·095	1·116	1·135	1·157	1·175	1·197	1·219	1·246	1·271	1·311	1·324	1·362	1·408	1·464	1·522
68	1·038	1·056	1·075	1·095	1·114	1·134	1·156	1·173	1·194	1·215	1·239	1·263	1·302	1·316	1·347	1·388	1·437	1·488
70	1·038	1·056	1·075	1·094	1·114	1·133	1·155	1·172	1·192	1·212	1·235	1·258	1·293	1·308	1·338	1·366	1·412	1·456
72	1·038	1·056	1·074	1·094	1·113	1·132	1·153	1·171	1·191	1·210	1·232	1·254	1·289	1·302	1·330	1·344	1·391	1·429
74	1·037	1·056	1·074	1·093	1·112	1·131	1·152	1·170	1·190	1·209	1·229	1·251	1·284	1·296	1·321	1·340	1·374	1·407
76	1·037	1·055	1·074	1·093	1·111	1·131	1·151	1·169	1·189	1·208	1·227	1·248	1·280	1·291	1·313	1·337	1·362	1·388
78	1·037	1·055	1·074	1·092	1·111	1·130	1·150	1·168	1·188	1·207	1·226	1·246	1·277	1·287	1·307	1·330	1·352	1·376
80	1·037	1·055	1·073	1·092	1·110	1·130	1·149	1·167	1·187	1·206	1·225	1·245	1·275	1·284	1·303	1·324	1·345	1·367
82	1·037	1·055	1·073	1·091	1·110	1·129	1·149	1·166	1·186	1·205	1·224	1·244	1·274	1·282	1·300	1·318	1·339	1·359

enter into the chambers, or between the single chambers, or in front of or behind the Gay-Lussac; in every case the *whole* of the gas is influenced in the same way, in spite of the view of many "practical" men differing from this. These considerations also apply to the action of the fan-blast spoken of *suprà* (pp. 735 *et seq.*).

Calculation of the Volume of Chamber-gases according to Temperature and Moisture.

In all calculations concerning chamber-gases it is not sufficient to take into account the difference of temperature and barometric pressure from the normal state of 0° and 760 mm., but the amount of moisture present in the chamber-atmosphere must be equally brought into the calculation. It is evidently impossible to do this on the assumption that the tension of aqueous vapour within the chambers is that ordinarily existing for any given temperature; the presence of sulphuric acid, not merely at the bottom but all over in the shape of mist, greatly changes the aqueous-vapour tension according to the varying strength of the acid. The tables of Regnault and Sorel, given on pp. 311 and 312, would admit of making the calculation in the proper manner; but it will be more convenient to consult the table on p. 779 (calculated by Sorel), which immediately gives the *volume occupied by a cubic metre* (or cubic foot) *of air, originally at* 0° *C. and* 760 *mm. pressure, after being brought into equilibrium of temperature and vapour-tension with dilute sulphuric acid of varying strength and temperature*, but without any change of pressure.